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**STUDY OF WEAR-PREVENTIVE PROPERTIES OF  
MACROCYCLIC COMPOUNDS FOR HIGH  
TEMPERATURE APPLICATION**

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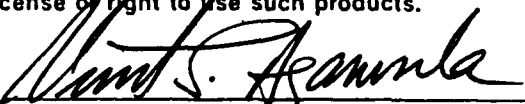
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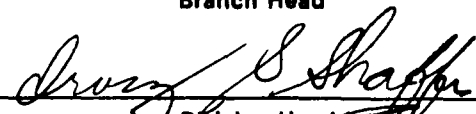
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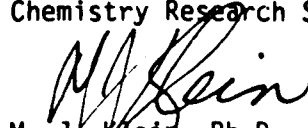
FOREWORD

This program has opened new areas of research in high temperature lubrication systems, based on metallo-organic macrocyclic compounds. After a critical review of the literature on the subject, and taking into consideration the requirements for wear and corrosion protection of bearings at elevated temperatures, eighteen compounds were chosen. A majority of the selected compounds were synthesized at IITRI, and a small number were obtained from a commercial source. All compounds were then characterized by Infrared (IR) and Nuclear Magnetic Resonance (NMR) methods to assure their formation and purity. All the eighteen compounds were then screened for their temperature stability by means of conventional thermo-oxidation tests. Based on these tests, eight compounds were identified that showed acceptable thermo-oxidation stability after exposure to 200°C for 1,000 hours. Test lubricant formulations were prepared by mixing the selected compounds with a high-temperature oil, viz., polysiloxane oil. The eight lubricant formulations were then examined for their thermo-oxidative stability and corrosion potential at 200°C for 1,000 hours using a standard bearing steel (AISI 52100). Analysis of the results of these tests led to a final selection of five grease formulations that exhibited thermal stability and corrosion protection better than a current high-temperature military grease. The five selected greases were then evaluated in the High Speed Bearing Tester (HSBT) that was designed and built for this program. The results of the wear tests showed that three of the five formulations exhibited wear protection properties that were equal to or surpassed that of a current (MILSPEC) grease. The compounds included in the three test formulations are as follows: (i) meso-tetraphenylporphyrin; (ii) copper chelate of phthalocyanine; and (iii) bis-salicylaldehydeethylenediimine, a schiff base. The grease formulations used in this research are based on a simple 5% addition of each of the selected compounds to the oil without any optimization. With optimization of the formulation involving the percent inclusion of the compound and the viscosity of the formulation it is felt that all the compounds would surpass the current (MILSPEC) grease.

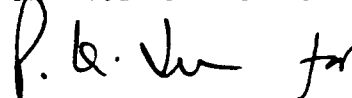
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TABLE OF CONTENTS

|  | <u>Page</u> |
|--|-------------|
| 1. BACKGROUND.....   | 1           |
| 1.1 State-of-the-Art of High Temperature Lubricants.....   | 1           |
| 1.1.1 Literature Review.....   | 1           |
| 1.1.1.1 Graphite as a Solid Lubricant.....   | 4           |
| 1.1.1.2 Graphite Fluoride.....   | 4           |
| 1.1.1.3 Non-Laminar Lubricants.....  | 5           |
| 1.1.1.4 Organic Solids as Lubricants.....  | 6           |
| 1.1.2 Conclusion.....  | 7           |
| 2. EXPERIMENTAL WORK AND RESULTS.....  | 11          |
| 2.1 Selection of Candidate Compounds.....  | 11          |
| 2.2 Synthesis of Schiff Bases and Their Metal Chelates.....  | 12          |
| 2.2.1 Schiff Base Derived From Salicylaldehyde<br>and Ethylenediamine.....                               | 12          |
| 2.2.2 Schiff Base of Salicylaldehyde and 4,4'-Benzidine.....   | 12          |
| 2.2.3 Schiff Base of Salicylaldehyde and 1,2-Phenylenediamine....  | 13          |
| 2.2.4 Schiff Base of Acetylacetone and Ethylenediamine.....  | 13          |
| 2.2.5 Preparation of Chelates From the Schiff Bases.....   | 13          |
| 2.2.5.1 Zn(II) Chelate of Bisacetylacetone-<br>ethylenediimine.....                                      | 13          |
| 2.2.5.2 Zn(II) Chelate of the Schiff Base Derived From<br>Bissalicylaldehyde and 4,4'-Benzidine.....     | 14          |
| 2.2.5.3 Cu(II) Chelate of the Schiff Base Derived From<br>Salicylaldehyde and 4,4'-Benzidine.....        | 14          |
| 2.2.5.4 Schiff Base Derived From Salicylaldehyde<br>and 1,3-Phenylenediamine.....                        | 15          |
| 2.2.5.5 Schiff Base Derived From 1,3-Phenylenediamine<br>and Acetylacetone.....                          | 23          |
| 2.2.5.6 Schiff Base Derived From Acetylacetone<br>and 1,2-Phenylenediamine.....                          | 23          |
| 2.2.5.7 Schiff Base Derived From Salicylaldehyde<br>and 1,2-Phenylenediamine.....                        | 24          |
| 2.2.6 Preparation of Cu(II) Chelates of Schiffs Bases.....   | 24          |
| 2.2.6.1 Cu(II) Chelate of Bissalicylaldehyde-<br>ethylenediimine.....                                    | 24          |
| 2.2.6.2 Copper Chelate of Schiff Base Derived From<br>Bissalicylaldehyde and 4,4'-Benzidine.....         | 25          |
| 2.2.6.3 Copper (II) Chelate of Schiff Base Derived From<br>Salicylaldehyde and 1,2-Phenylenediamine..... | 25          |
| 2.2.6.4 Cu(II) Chelate of the Schiff Base Derived From<br>Salicylaldehyde and 1,3-Phenylenediamine.....  | 26          |
| 2.2.6.5 Cu(II) Chelate of the Schiff Base Derived From<br>Acetylacetone and Ethylenediamine.....         | 26          |

## TABLE OF CONTENTS (Continued)

|  | <u>Page</u> |
|--|-------------|
| 2.2.6.6 Cu(II) Chelate of Schiff Base Derived From<br>Acetylacetone and 1,2-Phenylenediamine<br>Schiff Base..... | 26          |
| 2.2.6.7 Cu(II) Chelate of the Schiff Base From<br>Acetylacetone and 1,3-Phenylenediamine<br>Schiff Base.....     | 27          |
| 2.2.6.8 Cu(II) Chelate of the Schiff Base From<br>Acetylacetone and 4,4'-Benzidine<br>Schiff Base.....           | 27          |
| 2.3 Characterization of the Candidate Compounds by Infrared<br>and NMR Spectroscopic Methods.....                | 27          |
| 2.3.1 Infrared Spectral Method.....  | 37          |
| 2.3.2 Nuclear Magnetic Resonance Method (NMR).....   | 38          |
| 2.3.3 Spectral Analysis.....   | 40          |
| 2.3.3.1 Bissalicylaldehyde-4,4'-Benzidine Schiff Base.....   | 40          |
| 2.3.3.2 Schiff Base Derived From Salicylaldehyde<br>and 1,2-Phenylenediamine.....                                | 40          |
| 2.3.3.3 Schiff Base Derived From Acetylacetone<br>and Ethylenediamine.....                                       | 40          |
| 2.3.3.4 Copper Chelate of Schiff Base Derived From<br>Bissalicylaldehyde-4,4'-Benzidine.....                     | 41          |
| 2.3.3.5 Schiff Base Derived From Salicylaldehyde<br>and 1,3-Phenylenediamine.....                                | 41          |
| 2.3.3.6 Schiff Base of 1,3-Phenylenediamine<br>and Acetylacetone.....  | 41          |
| 2.3.3.7 Schiff Base of Acetylacetone<br>With 1,2-Phenylenediamine.....   | 41          |
| 2.3.3.8 Schiff Base of Salicylaldehyde<br>With 1,2-Phenylenediamine.....   | 42          |
| 2.3.3.9 Cu(II) Chelate of Bissalicylaldehyde-<br>ethylenediimine.....  | 42          |
| 2.3.3.10 Cu(II) Chelate of Schiff Base Derived From<br>Salicylaldehyde and 4,4'-Benzidine.....                   | 42          |
| 2.3.3.11 Cu(II) Chelate of Schiff Base Derived From<br>Salicylaldehyde and 1,2-Phenylenediamine.....             | 42          |
| 2.3.3.12 Cu(II) Chelate of Schiff Base Derived From<br>Salicylaldehyde and 1,3-Phenylenediamine.....             | 43          |
| 2.3.3.13 Cu(II) Chelate of Schiff Base Derived From<br>Acetylacetone and Ethylenediamine.....                    | 43          |
| 2.3.3.14 Cu(II) Chelate of Acetylacetone-1,2-<br>Phenylenediimine.....   | 43          |
| 2.3.3.15 Cu(II) Chelate of Acetylacetone-1,3-<br>Phenylenediimine.....   | 43          |

TABLE OF CONTENTS (Continued)

|  | <u>Page</u> |
|--|-------------|
| 2.4 Thermal Stability of the Candidate Compounds.....  | 43          |
| 2.4.1 Thermo-Oxidation Testing.....  | 43          |
| 2.4.2 Differential Scanning Calorimetric (DSC) Analysis<br>of Selected Schiff Bases and Their Cu <sup>+2</sup> Chelates..... | 49          |
| 2.5 Lubricant Formulation Using the Candidate Compounds.....   | 56          |
| 2.5.1 Thermo-Oxidation of Grease Formulations.....   | 57          |
| 2.6 Corrosion Testing.....   | 59          |
| 2.7 High Speed Bearing Test.....   | 63          |
| 2.7.1 Equipment Design.....  | 63          |
| 2.7.2 Test Procedures.....   | 68          |
| 2.8 Results.....   | 69          |
| 2.9 Failure Analysis.....  | 71          |
| 2.10 Recommendations.....  | 76          |
| APPENDIX 1.....  | 78          |



LIST OF FIGURES

| <u>Figure</u>   | <u>Page</u> |
|---|-------------|
| 1. Schiff bases of salicylaldehyde with ethylenediamine and benzidine.....  | 16          |
| 2. Schiff bases using acetylacetone as well as ethylenediamine.....   | 17          |
| 3. Schiff bases and zinc (II) chelate.....  | 18          |
| 4. Zn chelate of Schiff base obtained from salicylaldehyde and 4,4'-benzidine.....  | 19          |
| 5. Some copper chelates of Schiff bases.....  | 20          |
| 6. Porphyrins.....  | 21          |
| 7. Phthalocyanines.....   | 22          |
| 8. Formation of different Schiff base compounds.....  | 33          |
| 9. Thermally stable compounds selected for this research.....   | 47          |
| 10. Off-the-shelf (commercial) compounds used in this research.....   | 48          |
| 11. Photomicrographs of surface corrosion on samples of bearing steel, 52100, exposed to 200°C for 1,000 hr in air and various grease formulations..... | 62          |
| 12. Assembly drawing of bearing lubricant test fixture.....   | 64          |
| 13. Drawing of testing bearing holder.....  | 65          |
| 14. Overall view of high speed bearing tester.....  | 66          |
| 15. Side view of high speed bearing tester showing bearing assembly.....  | 67          |
| 16. Side view of bearing testing showing dead weight loading system.....  | 67          |
| 17. Surface appearance of balls taken from bearings tested at 200°C (390°F) in the High Speed Bearing Tester (HSBT).....                                | 72a         |
| 18. Welded spallation section on ball bearing.....  | 74          |
| 19. Surface film present on ball from bearing number 31.....  | 75          |

LIST OF TABLES

| <u>Table</u>  | <u>Page</u> |
|---|-------------|
| 1. Coefficient of Friction Using Metal-Free Phthalocyanine to Lubricate Oscillating Plain Bearing at Unit Stresses up to 25,000 P.S.I. and Temperatures to 649°C..... | 3           |
| 2. Friction Properties of Phthalocyanine Pigments at Moderate Levels.....   | 8           |
| 3. E. P. Effect of a Bromo-Chloro-Copper Phthalocyanine Pigment.....  | 8           |
| 4. Coefficient of Friction at Temperatures of -68°C to 816°C Using Metal-Free Phthalocyanine Lubricant in a Pendulum Bearing Machine.....                             | 9           |
| 5. List of Compounds Used in Thermal Stability Characteristic Tests.....  | 29          |
| 6. Infra Red Spectral Data for Compounds Investigated for High Temperature Stability Studies.....   | 30          |
| 7. Thermal and Oxidative (Air) Stability of Candidate Compounds.....  | 45          |
| 8. List of "Thermally Stable" Candidate Compounds.....  | 46          |
| 9A. Materials Analyzed by DSC.....  | 50          |
| 9B. Test Sample Designations.....   | 50          |
| 10. DSC Sample Weight Losses.....   | 51          |
| 11. DSC Sample Weight Losses at 200°C.....  | 53          |
| 12. Highlights of DSC Data of Candidate Compounds.....  | 55          |
| 13. Candidate Lubricant Formulations.....   | 58          |
| 14. Thermooxidation Tests of Base Compounds and Lubricant Formulations.....   | 60          |
| 15. Summary of Corrosion Tests on 52100 Steel Exposed to Air at 200°C.....  | 61          |
| 16. Summary of Data From High Speed (10,000 RPM) High Temperature (200°C Bearing Tester (1)).....   | 70          |
| 17. Summary of High Speed Bearing Tests.....  | 71          |

## 1. BACKGROUND

This research is concerned with the exploration of layer-lattice organic compounds of the macrocyclic-type as well as the Schiff-base class of compounds and their metal chelates for their application as high temperature lubricant additives as well as lubricants in their own right. On the basis of the molecular geometry, chemical structure, coordinate (chemical) bonding, electrochemical properties and thermal stabilities of the macrocyclic ligands such as the phthalocyanines and taking into consideration previous studies on their inclusion into high temperature grease compositions, it is felt that this class of compounds would be very valuable for application to problems unique to operating aircraft in naval environments. Further, it is considered that significant improvements could be achieved in this area in view of the fact that the chemical structures of the macrocyclic ligands are amenable to substitution reactions to yield a wide range of improved compounds suitable for application to high temperature lubrication. Therefore, a study aimed at investigating the selection, design and synthesis of this class of compounds and an examination of any possible relationship between the molecular structure and stability on the one hand and the lubricant performance on the other would be very valuable toward the development of one or more grease formulations for high temperature application in U.S. Naval Aircraft.

In order to select for this research study candidate compounds belonging to the class of macrocyclic (organic) compounds, it is important to take into consideration all the previous work carried out in this area. A computer search of the literature on the subject was done and the relevant publications on soap-based and non-soap-based greases including the ones involving inorganic and organic gelling agents were critically reviewed. A brief review on the subject is presented in this section.

### 1.1 STATE-OF-THE-ART OF HIGH TEMPERATURE LUBRICANTS

#### 1.1.1 Literature Review

Modern aircraft engines function at extremely high temperatures and this has necessitated the development of special synthetic lubricants. A few of

the demands made on lubricants and greases are: (1) low viscosity variations, (2) good lubricating properties over a wide range of temperatures, (3) chemical stability, and (4) stability against oxidative degradation.

Metal-free phthalocyanines are reported to have been used as lubricants at high temperatures ( $>800^{\circ}\text{C}$ ) especially with bearings. This has been attributed to both their thermal stability and high load-bearing capacity. These desirable properties could conceivably be due to a possible formation of strongly adhering "films" on metal surfaces. The strong adhesion arises due to the formation of chemical bonds between the metal centers and the coordinating groups (i.e., pyrrole nitrogens) of the metal-free phthalocyanine. Chief among the other commonly studied and used solid lubricants are: (1) molybdenum disulfide ( $\text{MoS}_2$ ) and (2) graphite. Data on these three classes of compounds are summarized in Table 1 for a comparison of their properties. Besides, the use of poly (metal phosphinates) have been explored as grease thickeners in base fluids such as polysiloxanes and perfluoropolyethers for high temperature applications.

Since 1930 research work on synthetic lubricants has resulted in the development of wide range of lubricants particularly organic lubricants involving polyethers, phosphoric acid esters, silicones and fluorinated esters. In addition, compounds such as the phthalocyanines (i.e., metal-free- and metal chelate forms) anthracene dyes such as Indranthine Blue have been found to exhibit good friction reduction characteristics. In the category of inorganic compounds, molten glass has been reported to exhibit satisfactory lubricating properties at temperatures  $>1200^{\circ}\text{C}$ . Some among the common inorganic lubricants reported in the literature are (i) molybdenum disulfide ( $\text{MoS}_2$ ) and (ii) fluorinated and free graphite. [H.E. Sliney; Lubr. Eng. 35, 497 1979]. However,  $\text{MoS}_2$  has been reported to be the compound of choice.  $\text{MoS}_2$  has a lamellar structure and it crystalizes with hexagonal symmetry and trigonal symmetry. On the Moh's scale its hardness ranges between 1.0 to 1.5 [A.R. Landsown,  $\text{MoS}_2$  Lubrication, ESTEC, Contract No. 1842/172]. The advantage of using  $\text{MoS}_2$  lies in (1) its chemical stability (ii) resistance to acids and (iii) impervious to radioactive radiation. It can be compressed by 40% at 120 Kbar pressure. It decomposes at  $1100^{\circ}\text{C}$  releasing Mo and sulfur under vacuum. Its lubricating properties are attributable to its crystal structure.

TABLE 1. COEFFICIENT OF FRICTION USING METAL-FREE  
 PHTHALOCYANINE TO LUBRICATE OSCILLATING PLAIN BEARING  
 AT UNIT STRESSES UP TO 25,000 P.S.I. AND TEMPERATURES TO 649°C

Bearing material: age-hardened S-Inconel

Shaft material: nitrided iron-base superalloy

Atmosphere: air

| Lubricant  | Bearing<br>Ambient<br>Temp.,<br>°F. | Bearing<br>Stress,<br>P.S.I. | Av.<br>Coefficient<br>of<br>Friction |
|--|-------------------------------------|------------------------------|--------------------------------------|
| Metal-free<br>phthalocyanine plus<br>polyisobutylene | Room                                | 5,000                        | 0.075                                |
|  | 1,000                               | 5,000                        | 0.01                                 |
|  | 1,000                               | 10,000                       | 0.035                                |
|  | 1,000                               | 15,000                       | 0.035                                |
|  | 1,000                               | 20,000                       | 0.05                                 |
|  | 1,000                               | 25,000                       | 0.055                                |
|  | Room                                | 5,000                        | 0.06                                 |
|  | 1,200                               | 5,000                        | 0.03                                 |
|  | 1,200                               | 10,000                       | 0.11                                 |
|  | 1,200                               | 15,000                       | 0.08                                 |
|  | 1,200                               | 20,000                       | 0.11                                 |
|  | 1,200                               | 25,000                       | 0.08                                 |
|  | 750                                 | 5,000                        | 0.08                                 |
|  | 750                                 | 10,000                       | 0.25                                 |
|  | -75                                 | 5,000                        | 0.23                                 |
| Molybdenum disulfide                                 | Room                                | 5,000                        | 0.01                                 |
|  | 750                                 | 10,000                       | 0.12                                 |
| Graphite   | Room                                | 5,000                        | 0.01                                 |
|  | 750                                 | 5,000                        | 0.07                                 |
|  | 750                                 | 10,000                       | 0.23                                 |
|  | 600                                 | 5,000                        | 0.05                                 |
|  | 600                                 | 10,000                       | 0.09                                 |
|  | 600                                 | 20,000                       | 0.08                                 |

Bearing assembly was disassembled after each 5,000 p.s.i. load increment and relubricated. Generally from 1,500 to 3,000 cycles of shaft motion occurred between relubrication intervals.

Specimen in good condition. Bearing exhibited slight galling at edges. "Slight galling". No damage after 20 cycles.  
 Bearing in good condition. "Galled". Support bearing failed.

Table 1 Taken from: H.H. Krause et al., J. Chem. Eng. Data, 6, 112-118 (1961).

In the sulfur layers in  $\text{MoS}_2$  the Van der Waals forces between the layers are weak permitting an easy movement of the lamella. This structural condition lowers the overall friction of the moving components. The ionic bond between Mo and S helps in resisting the penetration of sulfur asperities. Small amounts of  $\text{MoS}_2$  provide good lubrication properties to the surfaces in contact.

$\text{MoS}_2$  is applied under carefully controlled conditions i.e., (1) in an inert atmosphere and (ii) vacuum. The friction coefficient obtained is a function of the pressure at which the MoS is applied to the surface. A few of the limitations of  $\text{MoS}_2$  are: (1) fall in the friction coefficient and increase in wear in the presence of water and organic vapors; (2) readily attacked by oxygen at  $300^\circ\text{C}$  yielding molybdenum trioxide at  $400^\circ\text{C}$ . Under these conditions the adhesion of  $\text{MoS}_2$  is altered and hence its lubricating properties adversely affected.

Another molybdenum based lubricant is molybdenum silicide. This has good resistance to oxidation and functions as a lubricant up to temperatures of  $750^\circ\text{C}$ . [H.H. Krause et. al. J. Chem. Eng. data 6, 112 (1961)]

#### 1.1.1.1 Graphite as a Solid Lubricant

Like  $\text{MoS}_2$ , graphite is a lamellar solid having a layer-layer structure with a distance of 0.335 nm between layers. The low friction of graphite has been attributed to the low interatomic forces between the layers.

Graphite functions as a lubricant by depositing as a thin graphite film on the surface of the metal surface under investigation unlike  $\text{MoS}_2$  which adheres strongly to the surface of the metal. The graphite film lacks the strong adhesion characteristics of  $\text{MoS}_2$  [H.E. Sliney; ASLE TRANS 21, 109-117 ('78)]. In the presence of water, graphite has a favorable lubricating property as compared to that in the absence of water. [R.H. Savage; J. Appl. Phys. 19, (1948); ibid 27, 136 ('56)].

#### 1.1.1.2 Graphite Fluoride

Graphite fluoride obtained by the reaction of graphite with fluorine is represented by the molecular formula,  $(\text{CF}_x)_n$ . It has been known since 1934 and its utilization for lubrication purposes began only from 1969. The properties of this solid lubricant is critically dependent on the degree of fluor-

ination denoted by the term  $x$  in the above formula and the value of  $x$  ranges between 0.68 and 1.12. Structurally, graphite fluoride does not resemble that of graphite.  $(CF_x)_n$  has a condensed cyclohexane system in the chair conformation. It appears as a condensed "hydroaromatic" compound.

Comparative studies between graphite fluoride and  $MoS_2$  films with respect to lubricating properties at  $440^\circ C$  showed that graphite fluoride was superior. Graphite fluoride was stable up to  $873^\circ K$  and decomposed at  $1,073^\circ K$ . Several unsaturated fluorinated decomposition products were obtained in the neighborhood of  $1073^\circ K$ . Irrespective of the presence of water in the system,  $(CF_x)_n$  has shown improved performance characteristics with increased incorporation of fluorine. [R. Fusaro et. al.; ASLE TRANS 13, 56-65 (1970); ibid 20, 15-24, ('77)]. Further, friction coefficients were independent of fluoride content. The nature of the surface being coated has an effect on the wear and lubricating capabilities. [Once the surface has been penetrated, the adherent film provides prolonged protection by providing the  $(CF_x)_n$  layer] [H.E. Sliney: ASLE TRANS. 21, 109-112 ('88)]. Examination of residual  $(CF_x)_n$  has shown that the formation of ionic  $F^-$  and hence  $(CF_2)_n$  may function chemically as an active additive.

In addition to the above, other solid layer lattice lubricants have been studied and investigated. An example is boron nitride. The method of choice for synthesizing boron nitride is by the procedure of O'Connor [JACS 84, 1753-1754 (1962)]. According to this procedure, orthoboric acid is treated with urea. The resulting boron nitride upon thermal treatment is converted to a layer lattice structured compound. It is structurally similar to graphite. Boron nitride has high friction compared to graphite.

#### 1.1.1.3 Non-Laminar Lubricants

Apart from the layer-lattice lubricants mentioned above, other types of materials have been investigated. These range from plastics, inorganic powders which have different crystal structures, and finally composites and alloys. Studies by Bowen [AISE TRANS. 5, 315-326 (1962)] demonstrated that self lubricating composites shown below performed satisfactorily in high vacuum. (1) PTFE-glass fiber- $MoS_2$ , bronze-PTFE- $MoS_2$ , and Ag-PTFE- $WSe_2$  gave satisfactory results at  $160^\circ F$ . Of these the bronze-PTFE- $MoS_2$  proved to be the best with very little wear. This study showed that for the lowering of friction

and good lubrication one need not be limited to compounds having layer lattice structures only. (PTFE refers to polytetrafluoroethylene.)

Investigations of inorganic compounds with respect to their shear properties were carried out by Peterson et al. [AISE TRANS. 2, 225-234 (1959)] who showed that protection occurred by agglomeration into continuous films with respect to  $\text{PbO}$ ,  $\text{MoO}_3$ ,  $\text{WO}_3$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{CdO}$ ,  $\text{Cu}_2\text{O}$ , and  $\text{SnO}$ . Studies on the effect of temperature on lubricating properties showed that protection against wear improved with increase in temperature and fell with the lowering of temperature. This indicated that the shear processes and properties of the lubricant played a critical role in providing protection against wear [S. L. Cosgrove et al., ASLE TRANS. 2, 217-224 (1959)]. They showed that both  $\text{PbO}$  and  $\text{Ag}_2\text{S}$  were good at providing lubrication and protection against wear. The above provide a very brief overview of some of the lattice and non-lattice compounds which have been investigated and the conclusion arrived at is that  $\text{MoS}_2$  and graphite provide the best possible lubrication and protection against wear.

#### 1.1.1.4 Organic Solids as Lubricants

Several organic compounds have been utilized as lubricants, e.g., soaps and free fatty acids. The coatings of solids occur as macroscopic coatings while with the soaps and related compounds surface-adsorbed films are formed and thus provide protection on a molecular level. The latter can also be applied as a microscopic coating but suffer from the fact that they can be used only as single applications and fail thereafter.

Other useful organic lubricants reported in the literature are the polyimides and phosphorous-containing polyimides [B. S. Rao and I. K. Vera, Die Angew. Makromol Chemie 85, 149-158 (1980); R. L. Fusaro, ASLE TRANS. 21, 125-133 (1978)]. The major non-polymeric lubricants examined in earlier researches are the phthalocyanines and porphyrins.

Structurally phthalocyanines are lamellar in nature and meet one of the essential criteria for being a good lubricant. Several halogenated phthalocyanines and copper phthalocyanines have been investigated by Krause et al. [J. of Chem. and Eng. Data 6, 112-118 (1961)].



Investigations by Menter [Proc. Royal Soc. Lond., A 236, 119-135 (1956)] showed that Pt-phthaloyacynine had an interlamellar spacing of 1.2 nm. The thermal stability of metal-free phthalocyanines is good as indicated by insignificant darkening of the compound at 454°C. Decomposition occurs at ~538°C yielding  $\text{NH}_3$  and  $\text{N}_2$ . They sublime under vacuum at 510°C without decomposition. From the thermal stability factors, phthalocyanines prove to be very effective lubricants at elevated temperatures (800°C-900°C). The observed lubricating ability is conceivably a function of the layered structure of metal-free phthalocyanines. Comparative studies by Krause et. al have shown that metal-free phthalocyanines provide much better lubrication by virtue of their strong chelate binding to the metal surface. This type of surface-binding will not be favored in the case of metal-chelated phthalocyanines or the metallo-porphyrins. Hence they function as poor lubricants. However, this observation has been contradicted by the Salomon et. al [Wear 10, 383-396 ('67)] who showed that Copper phthalocyanine provided protection and lubrication similar to that by  $\text{MoS}_2$  (Tables 2 and 3). Phthalocyanines provide better protection as compared to graphite (Table 4). The duration of lubrication provided by various solid lubricants is given in Tables 2 and 3. It is seen that phthalocyanines function as lubricants better and for far longer periods as compared to natural graphite but not as well as  $\text{MoS}_2$ . See data shown in Table 2 [Wear 10, 383-391 ('67)]. Table 4 provide a comparison of the lubrication and wear protection afforded by phthalocyanines, graphite, graphite fluoride,  $\text{MoS}_2$  and  $\text{PbO}$ . [Krause, H.H. et al., J. Chem. Eng. Data, 6, 112-118 (1961)].

#### 1.1.2 Conclusion

A critical review of the past investigations of high temperature lubricants, more particularly the ones involving organic gelling agents, indicate that the studies carried out so far on phthalocyanines were largely of an exploratory nature and that there exists considerable scope for highly fruitful and profitable research in the direction of appropriate structural modification of porphyrins, phthalocyanines and their metal chelates that would suit the requirements of the different lubricants. Further, little research, if any, has been undertaken on another very important class of chemical compounds known as Schiff Bases (and their metal chelates) whose molecular structures exhibit square planar geometry. Monomeric and polymeric Schiff bases and

TABLE 2. FRICTION PROPERTIES OF PHTHALOCYANINE PIGMENTS AT MODERATE LOADS

Pin and ring machine; 1 m/sec; dry air; loading at intervals  
of 2 min load 14 kg

| Solid Powder |                             | Friction Coefficient $f$ |          |                 |
|--------------|-----------------------------|--------------------------|----------|-----------------|
| Group        | Type                        | Beginning                | End      | Time to Failure |
| A            | natural graphite            | 0.3                      | 0.5      | minutes         |
|              | metal-free                  | 0.3                      | 0.4      | 4 h             |
| B            | copper complex              | 0.2                      | 0.3-0.4  | minutes-3 h     |
| C            | copper-chloro complex       | 0.1-0.15                 | 0.25-0.4 | about 2 h       |
| D            | copper-chloro-bromo complex |                          |          |                 |
|              | 3 YS (Cl:Br = 1:1.3)        | 0.1                      | 0.3      | about 2 h       |
|              | 6 YS (Cl:Br = 1:4)          | 0.15                     | 0.20     | about 12 h      |
|              | MoS <sub>2</sub>            | 0.07                     | 0.03     | 6 - 1 h         |

TABLE 3. E. P. EFFECT OF A BROMO-CHLORO-COPPER PHTHALOCYANINE PIGMENT

Conditions as in Table 1, but load 62 kg Lubricant, MoS<sub>2</sub>;  
additive, Monastral fast green 7 YS

| Atmosphere | Additive (%) | Friction, $f$ |       | Friction Record       |                         | Statistical Significance of difference MoS <sub>2</sub> and Pigment |
|------------|--------------|---------------|-------|-----------------------|-------------------------|---|
|            |              | Initial       | Final | (a) Smooth Period (h) | (b) Time to Failure (h) |   |
| Dry air    | 0            | 0.06          | 0.04  | 6±1                   | 6.5 ± 1.5               |   |
|            | 3            | 0.08          | 0.08  | 10±3                  | 17±3                    | (b) significant   |
|            | 10           |               | 0.06  | 8.5±1                 | 12.5±4                  | (a) and (b) perhaps significant                                     |
| Dry oxygen | 0            | 0.07          | 0.05  | 3±1                   | 5±1                     |   |
|            | 3            | 0.06          | 0.04  | 4.5±1                 | 8±2                     | (a) and (b) not significant   |

Tables 2 and 3 Taken From: G. Solomon et al., Wear, 10, 383-396 (1967).

TABLE 4. COEFFICIENT OF FRICTION AT TEMPERATURES OF -68°C TO 816°C  
USING METAL-FREE PHTHALOCYANINE LUBRICANT IN A PENDULUM BEARING MACHINE

Bearing material: age-hardened S-Inconel  
Shaft material: nitrided iron-base superalloy  
Atmosphere: air

| Lubricant   | Bearing<br>Ambient<br>Temp.,<br>°C | Av.<br>Coefficient<br>of<br>Friction | Surface Appearance           |
|---|------------------------------------|--------------------------------------|------------------------------|
| None  | Room                               | 0.45                                 | Some scoring                 |
| None  | 538                                | 0.44                                 | Burnished                    |
| None  | 649                                | 0.40                                 | Burnished                    |
| Metal-free  | 427                                | 0.038                                | Burnished                    |
| phthalocyanine  | 538                                | 0.065                                | Burnished                    |
| plus polyisobutylene  | 649                                | 0.29                                 | Burnished, slight<br>galling |
|   | 816                                | 0.40                                 | Burnished, spalled           |
|   | -68                                | 0.21                                 | No damage                    |
| Copper phthalocyanine   | 427                                | 0.30                                 | Slightly galled              |
| Lead monoxide   | 538                                | 0.27                                 | Slightly galled              |
|   | 816                                | 0.26                                 | Burnished                    |
| Graphite plus<br>chlorofluorocarbon<br>$\text{C1}(\text{CF}_2\text{CFC1})_4\text{C1}$             | 316                                | 0.14                                 | Slightly galling             |
| Molybdenum disulfide<br>plus chlorofluorocarbon<br>$\text{C1}(\text{CF}_2\text{CFC1})_4\text{C1}$ | 316                                | 0.15                                 | Slight scoring               |

Table 4 Taken from: H.H. Krause et al., J. Chem. Eng. Data, 6, 112-118  
(1961).

their metal chelates have been reported to show chemical and thermal stability. It is therefore the objective of this research to investigate the two classes of compounds, i.e., (i) macrocyclic compounds of the type, porphyrins and phthalocyanines and (ii) planar polydentate ligands of the Schiff Base type.

## 2. EXPERIMENTAL WORK AND RESULTS

### 2.1 SELECTION OF CANDIDATE COMPOUNDS

On the basis of a critical review of the literature on the subject, the following compounds have been selected as being appropriate for our investigation:

#### A. Phthalocyanines

- (i) metal-free phthalocyanine
- (ii) Copper (II) - phthalocyanine
- (iii) Nickel (II) - phthalocyanine
- (iv) Nickel (II) - phthalocyanine (Tetra-sulfonic acid - Na -salt)
- (v) Fluorochrome phthalocyanine

#### B. Porphyrins

- (i) Meso-tetraphenyl porphyrin
- (ii) Hematoporphyrin

#### C. Schiff Bases

- (i) Bis-salicylaldehyde-ethylenediimine
- (ii) Bis-salicylaldehyde - benzidine
- (iii) Bis-salicylaldehyde - 1,2-diiminobenzene
- (iv) Bis-salicylaldehyde - 1,3-diiminobenze
- (v) Bis-acetylacetoneethylenediimine
- (vi) Cu (II), Ni (II) and Zn (II) chelates of the above Schiff bases

The metal-free phthalocyanine and its copper chelate are included in this research in order to provide comparison. They have both been investigated earlier and some data on their performance in lubricants are available. The rest of the phthalocyanines and porphyrins included in the above list are "off-the-shelf items", which were obtained commercially.

The five Schiff Bases and their metal chelates of Copper (II), Nickel (II) and Zinc (II) shown above in the list of selected compounds were synthesized and characterized in our (IITRI) laboratories. The synthetic procedures employed and the chemical structures of the selected compounds are presented in this section.

## 2.2 SYNTHESIS OF SCHIFF BASES AND THEIR METAL CHELATES

### 2.2.1 Schiff Base Derived From Salicylaldehyde and Ethylenediamine

#### Chemicals

1. Salicylaldehyde = 12.12 g (0.1 mole)
2. Ethanol = 50 mL
3. Ethylenediamine = 3.0 g.

Into a clean and dry three-necked flask, nitrogen gas is flushed to maintain anhydrous conditions. To this, salicylaldehyde (12.212 g; 10.66 m moles) was transferred. This was followed by the addition of ethanol (50.0 mL). The mixture was stirred and warmed to 60°C. An ethanolic solution of ethylenediamine [3.0 g of ethylenediamine in ethanol (20.0 mL)] was added dropwise. The reaction then proceeded vigorously. After warming for 1 hour the reaction mixture was allowed to cool down to room temperature to yield a solid product.

Yield = 13.864 g  
Yield % = 100.0  
M.P = 122 - 123C

### 2.2.2 Schiff Base of Salicylaldehyde and 4,4'-Benzidine

#### Chemicals

1. Salicylaldehyde = 6.176 g
2. Ethanol = 25.0 mL
3. 4,4' Benzidine = 4.8824 g
4. DMF:EtOH 1:1 = 50 mL

#### Procedure:

To a stirred solution of salicylaldehyde (6.176 g) in ethanol (25.0 mL) in a dry, three-necked flask was added 4,4'-benzidine (in 50 mL of DMF:EtOH solvent mixture) dropwise. The reaction mixture was warmed to 60°C for two hours and kept stirring overnight at room temperature when a solid product was obtained. The solid was filtered and washed with ethanol to remove any starting materials. It was dried under vacuum at 50° for several hours.

Yield = 9.391 g  
yield % = 100

### 2.2.3 Schiff Base of Salicylaldehyde and 1,2-Phenylenediamine

#### Chemicals

1. Salicylaldehyde = 12.212 g (10.656 mL)
2. 1,2-Phenylenediamine = 5.407 g
3. Ethanol = 25 mL

In a 100 ml three necked flask, salicylaldehyde (12.212 g, 0.1 mole, 2 equiv. w.r.t the base) was taken and an atmosphere of nitrogen maintained. To this an ethanolic solution of 1,2-phenylenediamine (5.407 gm, 1-equiv. w.r.t. salicylaldehyde) was added dropwise. At the end of the addition, the mixture was stirred for 2 hours at 60°C and then at room temperature overnight. A solid yellow orange compound was obtained.

Yield = 14.48 g

### 2.2.4 Schiff Base of Acetylacetone and Ethylenediamine

#### Chemicals

1. Acetylacetone = 10.14 g (10.4mL; 0.1 mole)
2. Ethylenediamine = 3.0 g (3.34 mL)
3. Ethanol = 25.0 mL

#### Procedure:

In a 3-necked flask (100 mL) acetylacetone (10.14 g) was taken and kept stirring under nitrogen. To this an ethanolic solution of ethylenediamine (3.0 g in ethanol 25 mL) was added dropwise at room temperature. The reaction mixture was kept stirring at room temperature overnight. A pale cream-colored solid was obtained.

Yield = 11.1 g

Yield % = 79%

### 2.2.5 Preparation of Chelates From the Schiff Bases

#### 2.2.5.1 Zn(II) Chelate of Bisacetylacetoneethylenediimine

#### Chemical

1. Schiff base derived from acetylacetone and ethylene diamine = 2.24 g
2. Zn (OAC)<sub>2</sub>.2H<sub>2</sub>O = 2.4584 g

In a 3-necked flask (100 mL), the Schiff base (2.24 g; 0.01 mole) in methanol (10.0 mL) was stirred under nitrogen at room temperature. Zn

(OAc)<sub>2</sub>.2H<sub>2</sub>O (2.485 g; 0.0112 mole) in methanol (20.0 mL) was warmed till all solids went into solution. The warm solution of Zn(OAc)<sub>2</sub>.2H<sub>2</sub>O was added in one lot to the methanolic solution of the Schiff base and the reaction mixture was maintained at 60° for 4 hours and then left overnight at room temperature when a grey powdery solid was obtained. The solvent was stripped off, the solid was washed with ethanol and dried under vacuum at 60° for several hours.

2.2.5.2 Zn(II) Chelate of the Schiff Base Derived From Bissalicylaldehyde and 4,4'-Benzidine

Chemicals

1. Schiff base derived from salicylaldehyde and 4,4'-benzidine = 391 mg
2. Zn (OAc)<sub>2</sub>.2H<sub>2</sub>O = 245.84 mg

Procedure:

In a clean and dry three-necked flask (500 mL), 200 mL of dimethyl formamide (DMF) was warmed to 100° under nitrogen. The Schiff's base (391.0 mg, 0.001 mole) was added in small lots till a clear solution was obtained. A warm methanolic solution of Zn (OAc)<sub>2</sub>.2H<sub>2</sub>O (245.84 mg, 0.0012 moles; 5 ml MeOH) was added to the above solution. The reaction mixture was maintained at 100°C for three hours. A solid compound separated after the Zn (OAc)<sub>2</sub>.2H<sub>2</sub>O was added, indicating the formation of the chelate. The reaction mixture was kept stirring overnight at room temperature. Subsequent work-up consisted of stripping the reaction mixture of the DMF and reducing the volume to a small volume (ca 10.0). The product in DMF was diluted with ether (50.0 mL), filtered, washed with more ether and dried under vacuum at 60° for several hours.

2.2.5.3 Cu(II) Chelate of the Schiff Base Derived From Salicylaldehyde and 4,4'-Benzidine

Chemicals

1. Schiff base of salicylaldehyde and -benzidine = 391.0 mg
2. Cu (II) Acetate monohydrate = 233.6 mg
3. DMF = 200.0 mL



Procedure:

The reaction and the work-up were performed exactly in the same manner as described in the preceding experiment. The reaction yielded the desired chelate as indicated by the formation of a solid precipitate and by the infra-red absorption spectra.

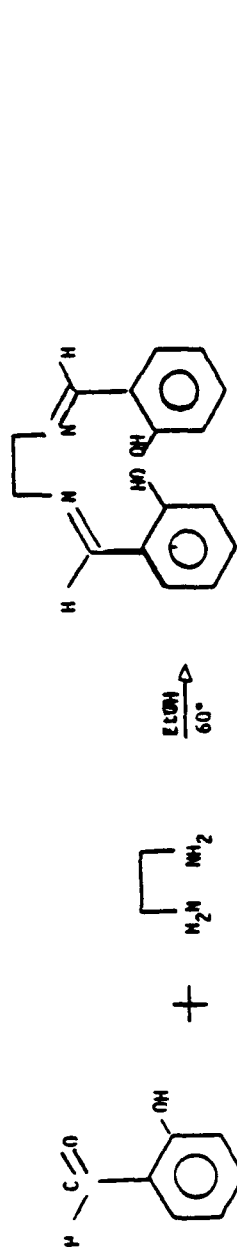
The reactions involved in the formation of the Schiff bases discussed above are represented structurally in Figures 1-5. The macrocyclic compounds obtained off-the-shelf are represented in Figures 6 and 7.

**2.2.5.4 Schiff Base Derived From Salicylaldehyde and 1,3-Phenylenediamine**

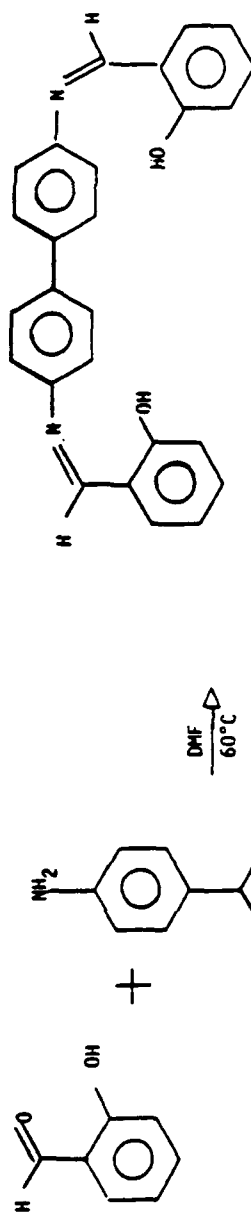
| Chemicals               | Amount                       |
|-------------------------|------------------------------|
| 1. Salicylaldehyde      | 30.0 g (26.18 mL) 0.246 mole |
| 2. 1,3-Phenylenediamine | 13.27 g 0.123 mole           |
| 3. Ethanol              | 150.0 mL                     |

Procedure:

A clean dry 3-necked flask was fitted with a condenser and pressure equilibrating separatory funnel. A stream of nitrogen was maintained throughout the reaction so as to achieve anhydrous conditions. The flask was charged with salicylaldehyde (freshly distilled; 30.0g, 0.246 mole, 26.18 mL). To this anhydrous ethanol (75.0 mL) was added and the contents were stirred. Next an ethanolic solution of 1,3-phenylenediamine (ethanol 75.0 mL; 1,3-phenylenediamine 13.27g, 0.12 moles) was added in a slow stream. The reaction mixture was warmed gradually to 60°C and held at this temperature for six hours. The product was allowed to cool to room temperature, when a solid yellow ppt. is obtained, which was the desired Schiff base. The material was filtered and the solid was washed with ethanol (4 x 20.0 mL) to remove any unreacted starting materials from the reaction product. The sample was dried at 50°C for several hours under vacuum.

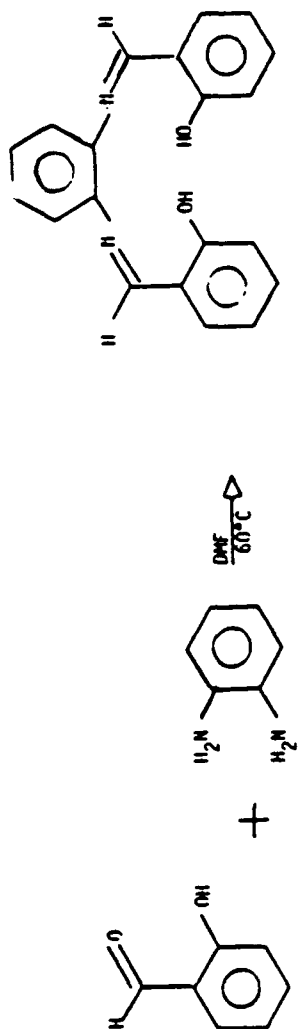


SCHIFF BASE FORMATION FROM SALICYLALDEHYDE AND ETHYLENEDIAMINE

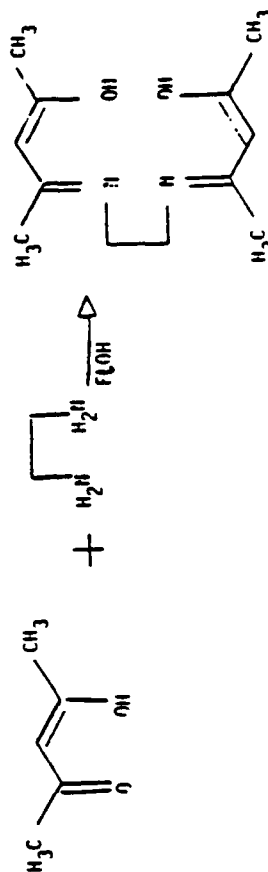


SCHIFF BASE FORMATION FROM SALICYLALDEHYDE AND 4,4'-BENZIDINE

Figure 1. Schiff bases of salicylaldehyde with ethylenediamine and benzidine.

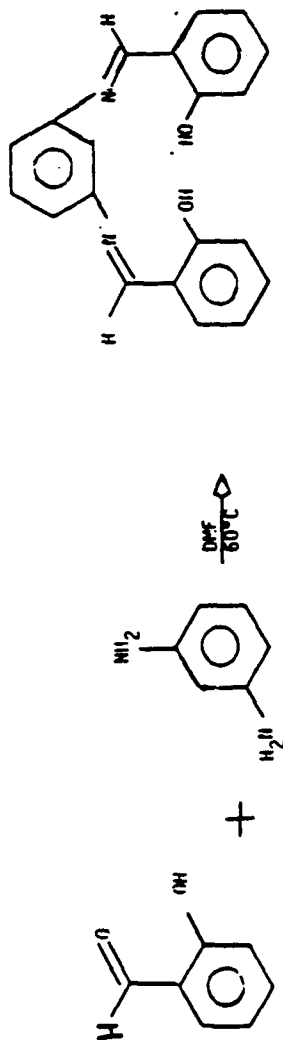


SCHIFF BASE FROM SALICYL ALDEHYDE AND 1,2-PHENYLENEDIAMINE

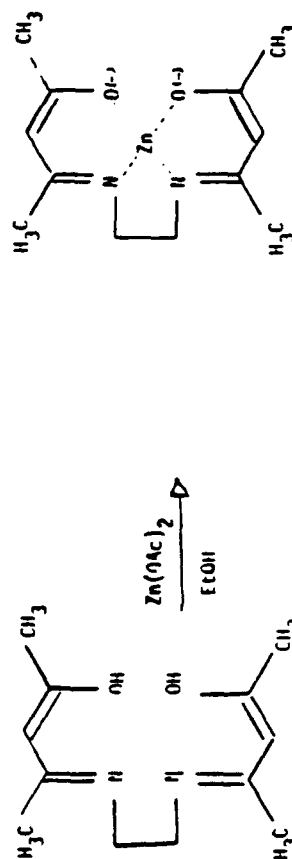


SCHIFF BASE FROM ACETYL ACETONE AND ETHYLENEDIAMINE

Figure 2. Schiff bases using acetylacetone as well as ethylenediamine.



SCHIFF BASE FORMATION FROM SALICYLALDEHYDE AND 1,3-PHENYLENEDIAMINE



ZN CHELATE FROM SCHIFF BASE OBTAINED FROM ACETYL ACETONE AND ETHYLENEDIAMINE

Figure 3. Schiff bases and zinc (II) chelate.

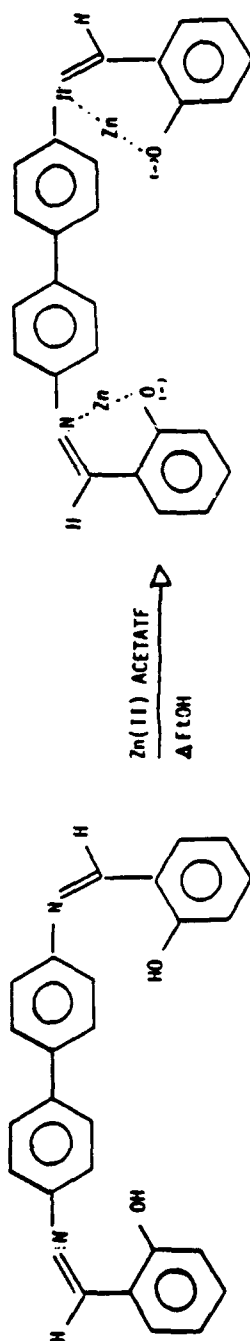
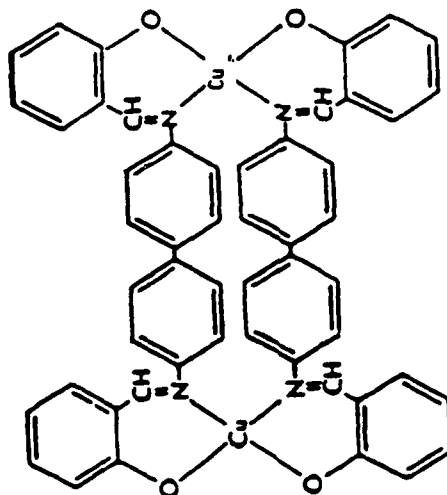
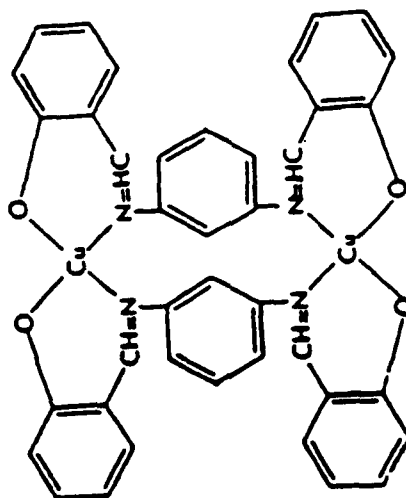


Figure 4. Zn chelate of Schiff base obtained from salicylaldehyde and 4,4'-benzidine.

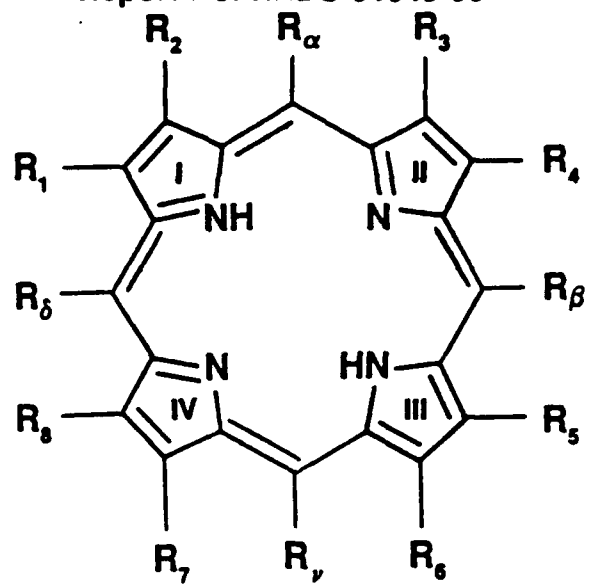


COPPER CHELATE OF SCHIFF BASE OBTAINED FROM  
SALICYLALDEHYDE AND 4,4'-BENZIDINE

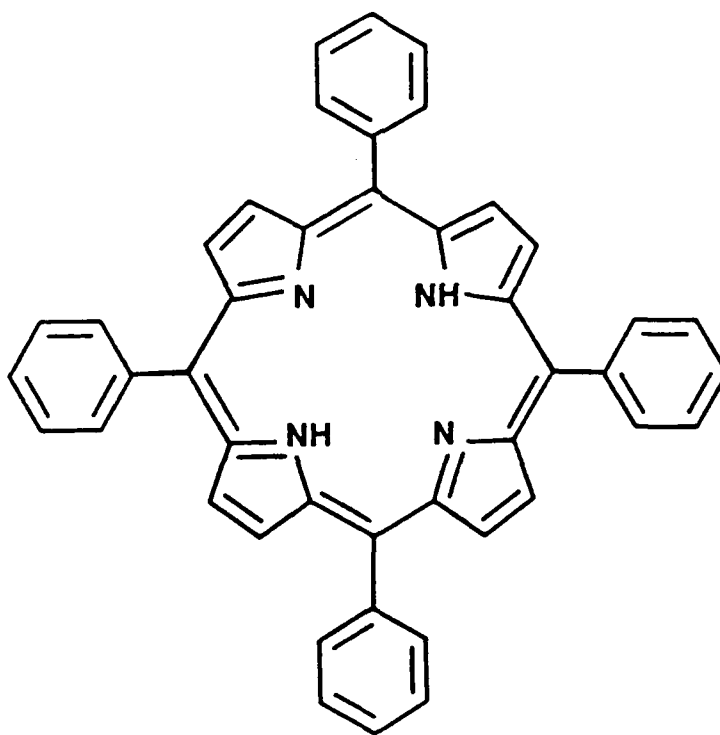


COPPER CHELATE OF SCHIFF BASE OBTAINED FROM  
SALICYLALDEHYDE AND 1,3-PHENYLENEDIAMINE

Figure 5. Some copper chelates of Schiff bases.

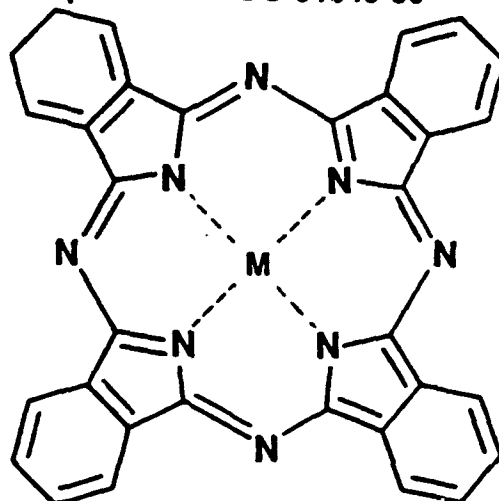


PORPHYRIN STRUCTURE WITH THE SUBSTITUENT POSITIONS

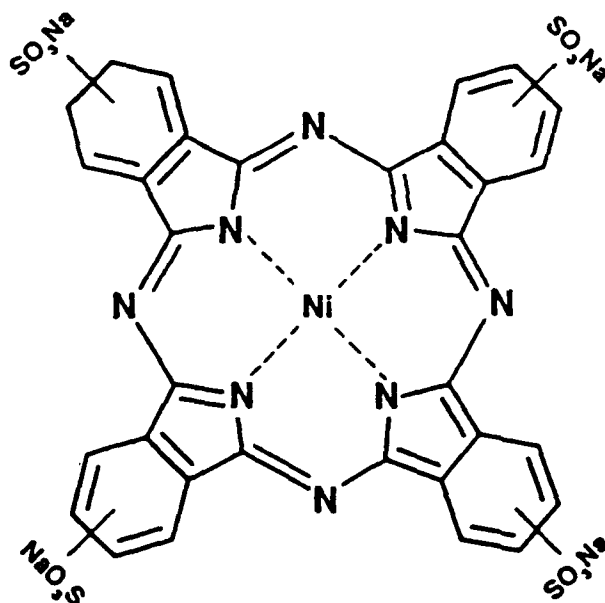


MESOTETRAPHENYL PORPHYRIN

Figure 6. Porphyrins



|                      |        |
|----------------------|--------|
| PHTHALOCYANINE       | (M=H)  |
| COPPER PHTHALOYANINE | (M=Cu) |
| NICKEL PHTHALOYANINE | (M=Ni) |



NICKEL PHTHALOCYANINE TETRASULFONIC ACID TETRA SODIUM SALT

Figure 7. Phthalocyanines



2.2.5.5 Schiff Base Derived From 1,3-Phenylenediamine and Acetylacetone

| Chemicals            | Amount                    |
|----------------------|---------------------------|
| Acetylacetone        | 10.0g (10.1 mL, 0.1 mole) |
| 1,3-Phenylenediamine | 5.4g (0.05 mole)          |
| Ethanol              | 50.0 mL                   |

Procedure:

The reaction was carried out in an atmosphere of nitrogen under anhydrous conditions. A clean dry two-necked flask fitted with a condenser and a pressure equilibrating separatory funnel was charged with acetylacetone (10.0 g, 10.1 mL, 0.1 mole) and diluted with anhydrous ethanol (20.0 mL) and mixed. This was followed by the slow addition of an ethanolic solution [30 mL (EtOH)] of 1,3-phenylenediamine (5.4g, 0.5 mole). The stirred reaction mixture was warmed to 60°C and held at this temperature for four hours. A solid material was obtained on cooling to room temperature. It was filtered and the solid was washed with ethanol (5 x 2.0 mL) so as to remove any unreacted starting material.

2.2.5.6 Schiff Base Derived From Acetylacetone and 1,2-Phenylenediamine

| Chemicals            | Amount            |
|----------------------|-------------------|
| Acetylacetone        | 10.0 g (0.1 mole) |
| 1,2-Phenylenediamine | 5.4 g.            |
| Ethanol              | 50.0 mL           |

Procedure:

The procedure described in the previous experiment was employed to obtain this Schiff base.

2.2.5.7 Schiff Base Derived From Salicylaldehyde  
and 1,2-Phenylenediamine

| Chemicals            | Amount  |
|----------------------|---------|
| Salicylaldehyde      | 12.212g |
| 1,2-Phenylenediamine | 5.407g  |
| Ethanol              | 50.0 mL |

The procedure developed in the previous experiment was employed for obtaining the above Schiff base without any modification. The yield of the product Schiff base was quantitative.

2.2.6 Preparation of Cu(II) Chelates of Schiff's Bases

2.2.6.1 Cu(II) Chelate of Bissalicylaldehydeethylenediimine

| Chemicals                         | Amount                                       |
|-----------------------------------|--|
| Salicylaldehyde                   | 18.3g (0.15 mole) (2 equiv. with the base)   |
| Ethylenediamine                   | 5.0 mL (4.49g, 0.075 mole)                   |
| Cu (II) acetate 1H <sub>2</sub> O | 60.0g (4 equiv. with respect to Schiff base) |
| Anhydrous DMF                     | 400.0 mL                                     |

Preparation of anhydrous DMF

DMF is distilled under a water aspirator pressure and the constant boiling fraction was collected. Molecular sieves (4A type) was dried under vacuum at 80°C overnight to remove any moisture and residual solvent. The distilled DMF was kept over the activated molecular sieves for 48 hours prior to use.

Procedure:

The reaction was performed under anhydrous conditions and in an atmosphere of nitrogen. A 3-necked flask was fitted with a reflux condenser and a pressure equalizing separatory funnel. To this, anhydrous DMF (300 mL) was added and stirred, followed by the addition of copper acetate monohydrate (60.0g). The contents were maintained at 60°C for 30 minutes and then salicylaldehyde (18.3g; 19.4 mL, 0.15 mole) was added in a slow stream. The

reaction mixture was kept stirring at 60°C for 15 minutes. At the end of this period, a DMF (100 mL) solution of ethylenediamine (5 mL) was added in a thin stream to the reaction mixture. After the addition was complete, the reaction was maintained at 60°C for six hours. During this period small amounts of the chelate precipitated out. The reaction mixture was cooled and filtered. The filtrate was discarded. It contained some unreacted Cu (II) acetate and the other starting materials. The solid Cu (II) chelate was washed with small amounts of DMF (5 x 10 mL), methanol and finally anhydrous ether (2 x 25.0 mL). The chelate was dried at 60°C under vacuum to remove the last traces of the solvent.

2.2.6.2 Copper Chelate of Schiff Base Derived From Bissalicylaldehyde and 4,4'-Benzidine

| Chemicals                        | Amount                     |
|----------------------------------|----------------------------|
| Salicylaldehyde                  | 4.8848 g (4.3 mL, 40 mole) |
| 4,4'-Benzidine                   | 3.6848 g (20 mole)         |
| Cu (II) acetate H <sub>2</sub> O | 8.0g                       |
| DMF                              | 100.0 mL                   |

Procedure:

The above procedure was utilized without incorporation of any modifications.

2.2.6.3 Copper (II) Chelate of Schiff Base Derived From Salicylaldehyde and 1,2-Phenylenediamine

| Chemicals                        | Amount  |
|----------------------------------|---------|
| Salicylaldehyde                  | 2.442 g |
| 1,2-Phenylenediamine             | 1.814 g |
| Cu (II) acetate H <sub>2</sub> O | 8.4 g   |

Procedure:

The previous procedure was utilized without incorporation of any modifications.

2.2.6.4 Cu(II) Chelate of the Schiff Base Derived From Salicylaldehyde and 1,3-Phenylenediamine

| Chemicals                          | Amount            |
|------------------------------------|-------------------|
| Salicylaldehyde                    | 6.106 g (5.25 mL) |
| 1,3-Phenylenediamine               | 2.7035 g          |
| Cu (II) acetate .1H <sub>2</sub> O | 10.0 g            |
| DMF                                | 200 mL            |

Procedure

The method developed in the previous procedure was utilized without any modifications and the desired chelate was obtained.

2.2.6.5 Cu (II) Chelate of the Schiff Base Derived From Acetylacetone and Ethylenediamine

| Chemicals                       | Amount          |
|---------------------------------|-----------------|
| Acetylacetone                   | 10.0g (10.3 mL) |
| Ethylene diamine                | 3.0g ( 3.34 mL) |
| Cu(II) acetate H <sub>2</sub> O | 20.0g           |
| DMF                             | 200 ml          |

Procedure:

The method developed previously was utilized without any modification and the desired chelate was obtained.

2.2.6.6 Cu(II) Chelate of Schiff Base Derived From Acetylacetone and 1,2-Phenylenediamine Schiff Base

| Chemicals                       | Amount                    |
|---------------------------------|---------------------------|
| Acetylacetone                   | 10.0g (10.3 mL; 0.1 mole) |
| 1,2-Phenylenediamine            | 5.3g (0.05 mole)          |
| Cu(II) acetate H <sub>2</sub> O | 19.8 g                    |
| DMF                             | 200 mL                    |

Procedures:

The method developed earlier was utilized without any modification to yield the designed chelates.

2.2.6.7 Cu(II) Chelate of the Schiff Base From Acetylacetone and 1,3-Phenylenediamine Schiff Base

| Chemicals                       | Amount                    |
|---------------------------------|---------------------------|
| Acetylacetone                   | 10.0g (10.3 mL, 0.1 mole) |
| 1,3-Phenylenediamine            | 5.3g (0.05 mole)          |
| Cu(II) acetate H <sub>2</sub> O | 19.8g                     |
| DMF                             | 200.0 mL                  |

Procedure:

The method described earlier was utilized without any modification to obtain the chelate in good yield.

2.2.6.8 Cu(II) Chelate of the Schiff Base Derived From Acetylacetone and 4,4'-Benzidine Schiff Base

| Chemicals                       | Amount   |
|---------------------------------|----------|
| Acetylacetone                   | 2.0 g    |
| 4,4'-Benzidine                  | 1.81 g   |
| Cu(II) acetate H <sub>2</sub> O | 4.00 g   |
| DMF                             | 40.00 mL |

Procedure:

The method described earlier was utilized without any modification to obtain the chelate.

2.3 CHARACTERIZATION OF THE CANDIDATE COMPOUNDS BY INFRARED AND NMR SPECTROSCOPIC METHODS

All the compounds synthesized in our laboratory and those which were commercially purchased for the present studies, have been examined by infrared (IR) and proton nuclear magnetic resonance (<sup>1</sup>H, NMR) spectroscopic techniques.

This has been carried out in order to elucidate the structure of each compound and thus confirm the presence of the projected compound in an unambiguous manner.

The basis of the study is the comparison of the IR and NMR spectrum of the starting material(s) along with those of the Schiff base(s) synthesized through the identification of spectroscopically-active functional groups (IR) and proton peak positions (NMR) present in the reaction product. Earlier in this report, we described the procedure developed for synthesizing both a few Schiff bases and some of their chelates with Zn (II) and Cu (II) metals. They are listed below.

Schiff base derived from salicylaldehyde and ethylenediamine  
Schiff base derived from salicylaldehyde and 4,4'-benzidine  
Schiff base derived from acetylacetone and ethylenediamine  
Schiff base derived from salicylaldehyde and 1,2-phenylenediamine

In addition, the zinc and copper chelates of the Schiff bases were synthesized and are listed below:

Zn (II) chelates of the Schiff Bases derived from:  
(i) salicylaldehyde and ethylenediamine;  
(ii) salicylaldehyde and 4,4'-benzidine; and  
Cu (II) chelate of the Schiff base derived from salicylaldehyde and 4,4'-benzidine

All the compounds synthesized and taken off the shelf for this research are listed in Table 5. IR-spectral data of the compounds are summarized in Table 6, and are also represented structurally in Figure 8. The alphabets shown against the different compounds listed in Table 5 refer to the reference number of the respective compounds which are used throughout this report. Zn (II) chelates are not listed in Table 6 since in our investigations, we used Cu (II) chelates only. This is because Zn (II) chelates exhibit tetrahedral (structural) geometry and hence would not conform to our major requirement, i.e., planar structure. They (i.e. Zn-chelates) are also not represented in Table 6, which provides the consolidated IR data of all the candidate compounds being investigated in this research.

TABLE 5. LIST OF COMPOUNDS USED IN THERMAL STABILITY CHARACTERISTICS TESTS

| Sample Identification | Reference in Log Book     | Chemical Description   |
|-----------------------|---------------------------|--|
| A                     | ** C06687-1               | Salicylaldehyde + Ethylenediamine                                  |
| B                     | ** C06687-3               | Salicylaldehyde + Benzidine  |
| C                     | ** C06687-4               | Acetylacetone + Ethylenediamine                                    |
| D                     | ** C06687-5               | Salicylaldehyde + 1,2-Phenylenediamine                             |
| E                     | ** C06687-11              | Cu(II) Chelate of (A)  |
| F                     | ** C6687-12               | Cu(II) Chelate of (D)  |
| G                     | ** C6687-13               | Cu(II) Chelate derived from Salicylaldehyde + 1,3-Phenylenediamine |
| H                     | ** C6687-14               | Cu(II) Chelate of (B)  |
| I                     | ** C6687-15               | Cu(II) Chelate of (C)  |
| J                     | ** C6687-16               | Cu(II) Chelate derived from Acetylacetone + 1,2-Phenylenediamine   |
| K                     | ** C6687-17               | Cu(II) Chelate derived from Acetylacetone + 1,3-Phenylenediamine   |
| L                     | ** C6687-18               | Cu(II) Chelate derived from Acetylacetone + Benzidine              |
| M                     | ** C6687-19               | Salicylaldehyde + 1,3-Phenylenediamine                             |
| N                     | ** C6687-20               | Acetylacetone + 1,3-Phenylenediamine                               |
| O                     | ** C6687-21               | Acetylacetone + 1,2-Phenylenediamine                               |
| P                     | Phthalocyanine (Kodak)    | Phthalocyanine (Kodak)   |
| Q                     | Phthalocyanine (Kodak)    | Cu(II) Phthalocyanine  |
| R                     | Mesotetraphenyl Porphyrin | Mesotetraphenyl Porphyrin  |

TABLE 6. INFRA RED SPECTRAL DATA FOR COMPOUNDS INVESTIGATED FOR HIGH TEMPERATURE STABILITY STUDIES

| Compound Identification | Spectral Peaks - IR Frequencies (in $\text{cm}^{-1}$ units) and Group Assignments  |   |
|-------------------------|--|---|
|                         | Room Temp.   | Experimental Conditions<br>48 hrs of heating at 200°C   |
| A                       | 1633, (C=N), 1574, 1497, 1367 (C-O)<br>1282, 1148, 1040, 1018, 855, 772, 746<br>( $\bar{o}$ subst. aromatics) $\text{cm}^{-1}$         | 1633 (C=N), 1574, 1495, 1369 (C-O)<br>1282, 1148, 1040, 855, 772, 746<br>( $\bar{o}$ substituted aromatic) $\text{cm}^{-1}$ |
| E                       | 1647 (C=N), 1626, 1597, 1331 (C-O) $\text{cm}^{-1}$  | 1606 (C=N), 1574, 1375 (C-O) $\text{cm}^{-1}$   |
| B                       | 1616 (C=N), 1574, 1496, 1361 (C-O) $\text{cm}^{-1}$  | 1616 (C=N), 1570, 1483, 1370 (C-O)<br>748 ( $\bar{o}$ substituted aromatic) $\text{cm}^{-1}$                                |
| H                       | 1607 (C=N), 1379 (C-O) $\text{cm}^{-1}$  |   |
| D                       | 1616 (C=N), 1556, 1481, 1371 (C-O)<br>1193, 761, 640, 578, 557, 530, 501 $\text{cm}^{-1}$  | 1626 (C=N), 1589, 1529, 1483, 1448,<br>1376 (C-O), 1313, 1273, 1251 $\text{cm}^{-1}$  |
| F                       | 1620 (C=N), 1525, 1446, 1378 (C-O),<br>1190, 1146, 1126, 1053, 978, 954<br>750, 733 ( $\bar{o}$ substituted aromatic) $\text{cm}^{-1}$ | 155 (C=N), 1448, 1387 (C-O), 750<br>733, 648, 617, 570, 499, 468 $\text{cm}^{-1}$   |
| M                       | 2368, 1616, (C=N) 1589, 1564, 1497, 1456<br>(C-O) 1283, 1194, 1150, 800, 754, 753,<br>688, 482 $\text{cm}^{-1}$                        | 1616 (C=N), 1566, 1460 (C-O) 1275,<br>1180, 1028, 960, 770 ( $\bar{o}$ subst.<br>aromatic) $\text{cm}^{-1}$                 |



TABLE 6. INFRARED SPECTRAL DATA FOR COMPOUNDS INVESTIGATED FOR HIGH TEMPERATURE STABILITY STUDIES  
(Continued)

| Compound<br>Identification | Spectral Peaks - IR Frequencies (in $\text{cm}^{-1}$ units) and Group Assignments |   |
|----------------------------|---|---|
|                            | Room Temp.  | Experimental Conditions<br>48 hrs of heating at 200°C     |
| G                          | 1605 (C=N), 1584, 1529, 1460, 1439,   | 1618 (C=N), 1531, 1466, 1385 (C-O), 756 $\text{cm}^{-1}$  |
|                            | 1379 (C-O), 1327, 1199, 1146, 978, 868  |   |
|                            | 756, 691, 538, 519, $\text{cm}^{-1}$  |   |
| C                          | 1614 (C=N), 1369 (C-O), 758, 738 $\text{cm}^{-1}$                                 | 2363, 2343, 1653 (C=O), 1599, 1433 (C-O) $\text{cm}^{-1}$ |
| I                          | 1581 (C=N), 1413, 1354 (C-O), 1275,   | 1576, 1551, 1410, 1352 (C-O), 1273, 1187,                 |
|                            | 1186, 1018, 935, 781, 684, 653, 613 $\text{cm}^{-1}$                              | 1185, 936, 779, 683, 651, 611, 452, 427 $\text{cm}^{-1}$  |
| O                          | 1632 (C=N), 1454, 1422, 1370 (C-O),   | 1650, 1608 (C=N), 1539, 1504, 1273,                       |
|                            | 1269, 1258, 1217, 1123, 1020, 882, 779,   | 1209, 1000, 825 $\text{cm}^{-1}$                          |
|                            | 764, 750 $\text{cm}^{-1}$   |   |
| J                          | 2363, 1570, 1548, 1521, 1398 (C-O) 1020,  | 1560, 1412, 1280 (C-O), 1016, 935, 779,                   |
|                            | 937, 780, 740, 684, 653, 613, 453 $\text{cm}^{-1}$                                | 736, 682, 653, 611, 455, 430 $\text{cm}^{-1}$             |
| N                          | 1664 (C=N), 1587, 1277 (C-O), 1178,   | 1616 (C=N), 1587, 1566, 1491, 1460, 1278,                 |
|                            | 1020, 999, 872 $\text{cm}^{-1}$   | 1180, 1142, 1028, 960, 908 $\text{cm}^{-1}$               |

TABLE 6. INFRARED SPECTRAL DATA FOR COMPOUNDS INVESTIGATED FOR HIGH TEMPERATURE STABILITY STUDIES  
(Continued)

| Compound<br>Identification | Spectral Peaks - IR Frequencies (in $\text{cm}^{-1}$ units) and Group Assignments     |  |
|----------------------------|---|--|
|                            | Room Temp.  | Experimental Conditions<br>48 hrs of heating at 200°C  |
| K                          | 1576, 1408, 1352 (C-O), 1275, 1136, 1017,<br>936, 779, 683, 654, 611 $\text{cm}^{-1}$ | 1618 (C=N), 1531, 1466, 1441, 1385,<br>1323 (C-O), 1249, 1202, 1151, 1024,<br>978, 925, 865, 835, 756 $\text{cm}^{-1}$ |
| P                          |   | 1439, 1338, 1317, 1302, 1273, 1118,<br>1093, 1001, 871, 750, 735, 729, 717,<br>613 $\text{cm}^{-1}$                    |
| Q                          |   | 1288, 1201, 1165, 1120, 1091, 1071,<br>899, 709, 725, 719 $\text{cm}^{-1}$   |
| R                          |   | 1597, 1466, 1403 $\text{cm}^{-1}$  |

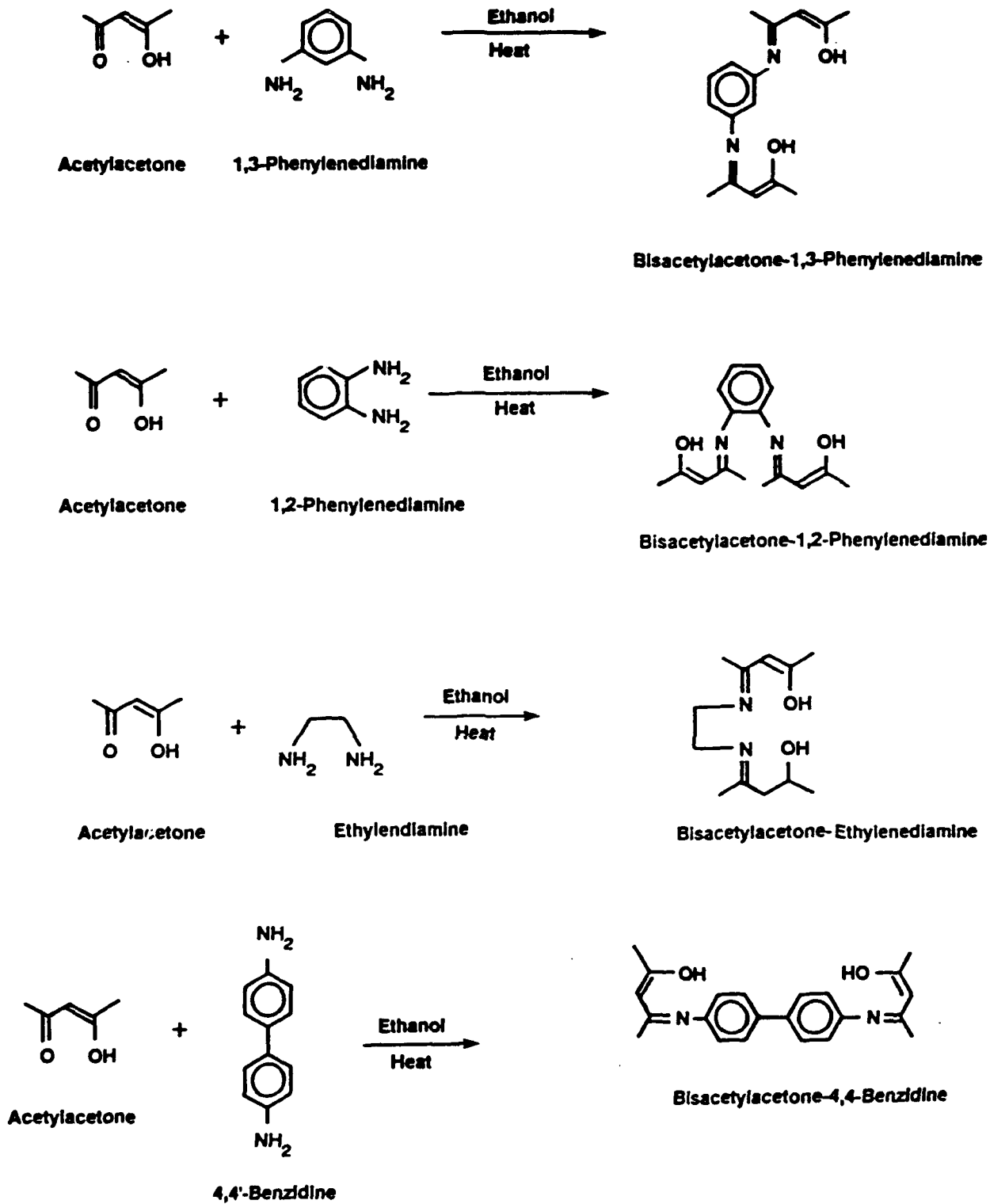


Figure 8. Formation of different schiff base compounds

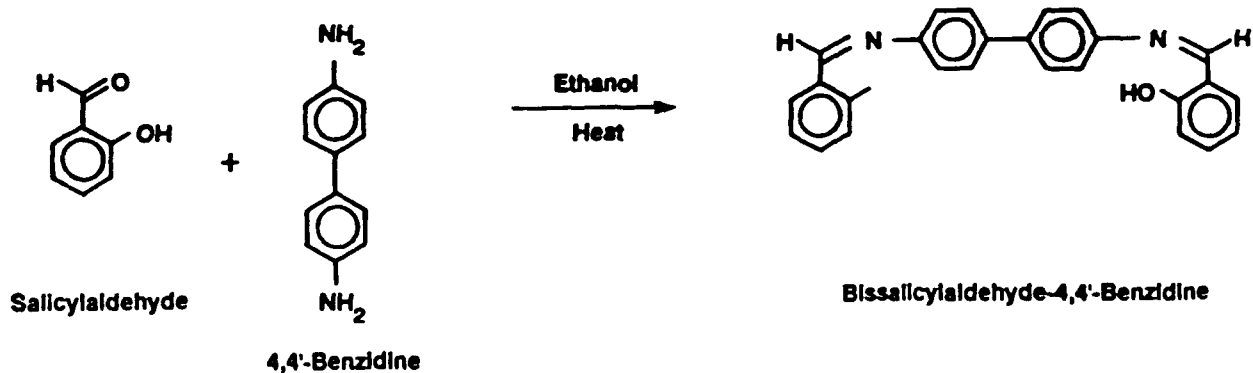
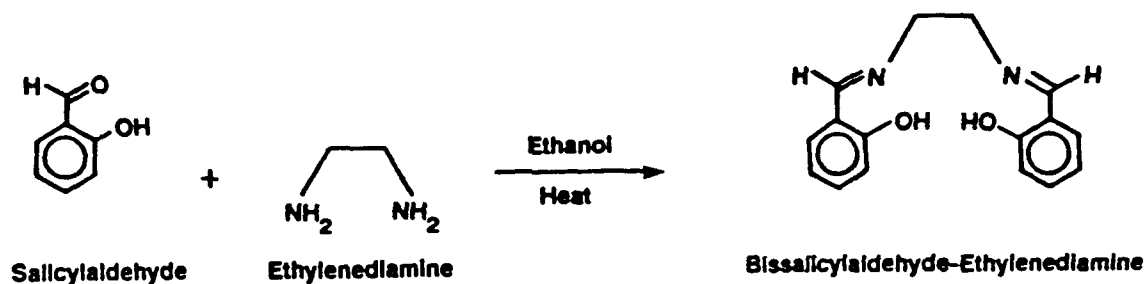
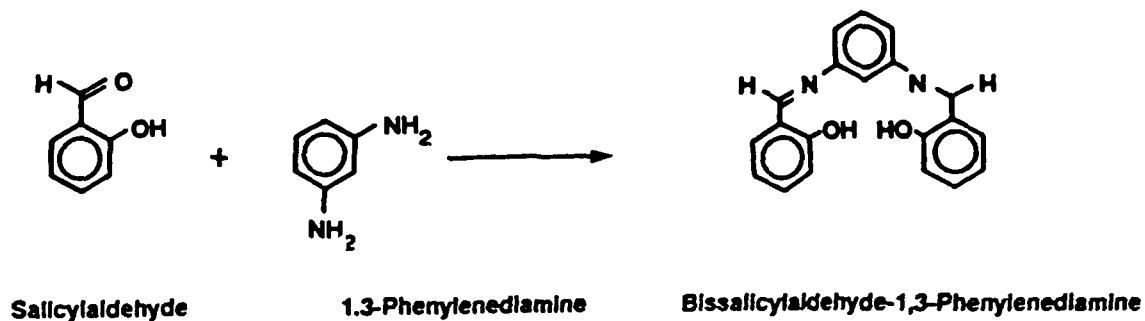
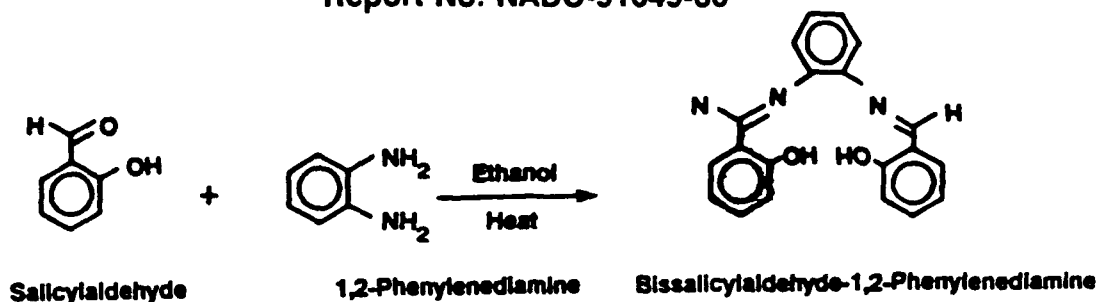


Figure 8. Formation of different schiff base compounds (Continued).

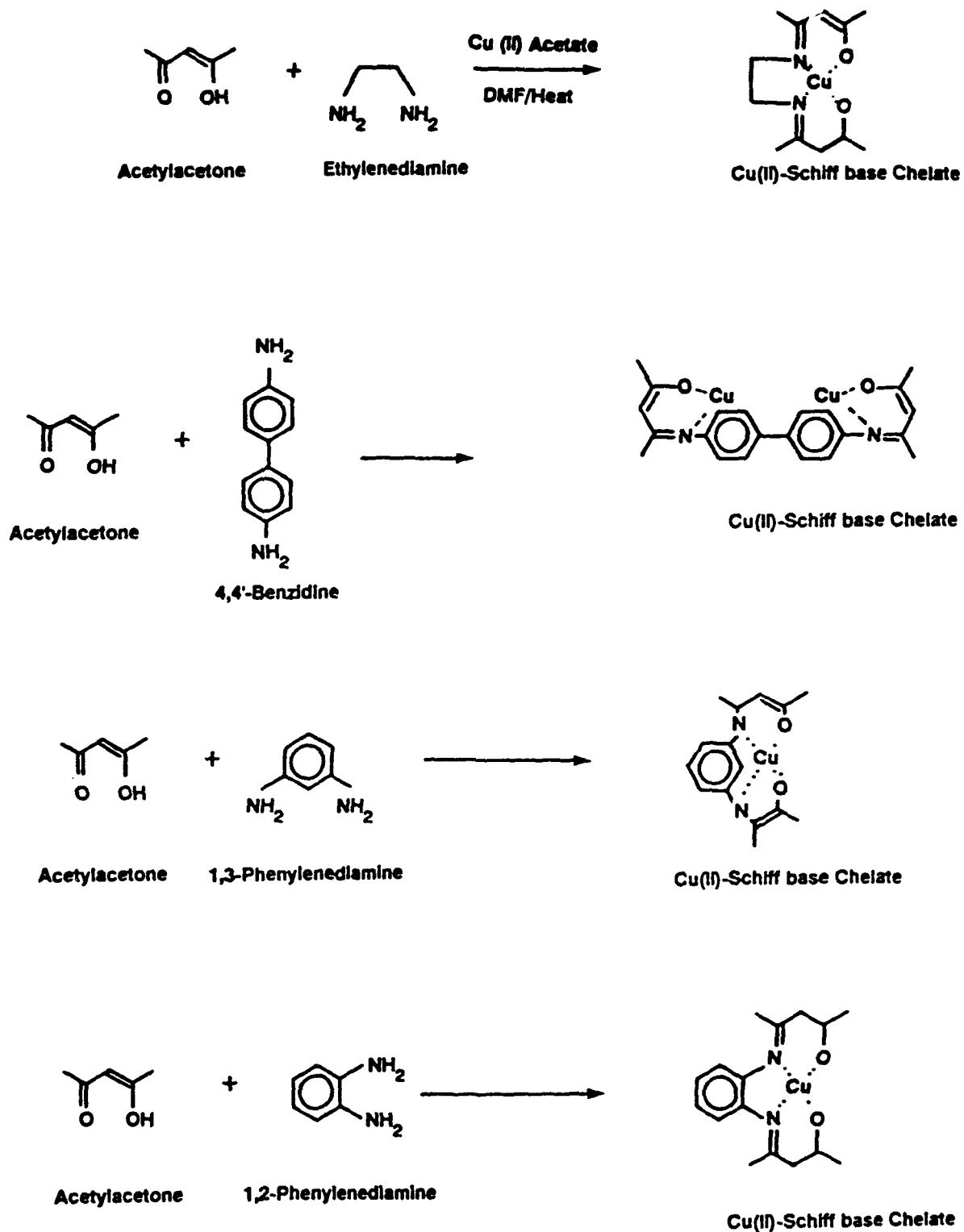


Figure 8. Formation of different schiff base compounds (Continued).

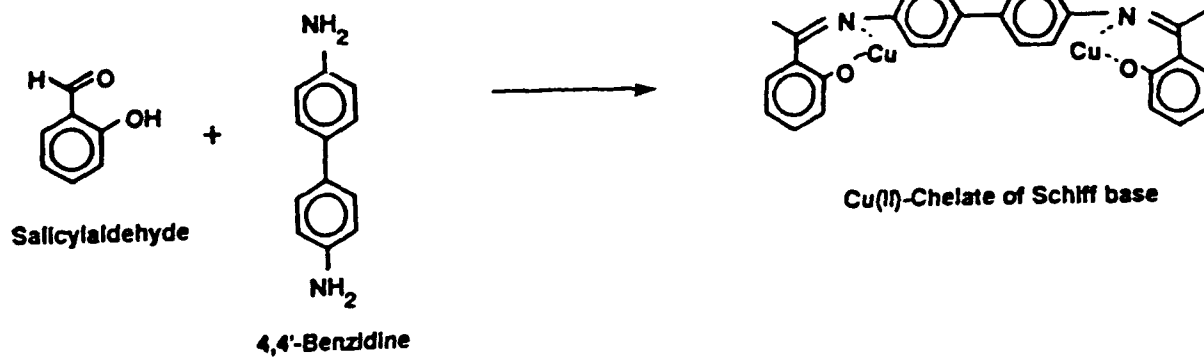
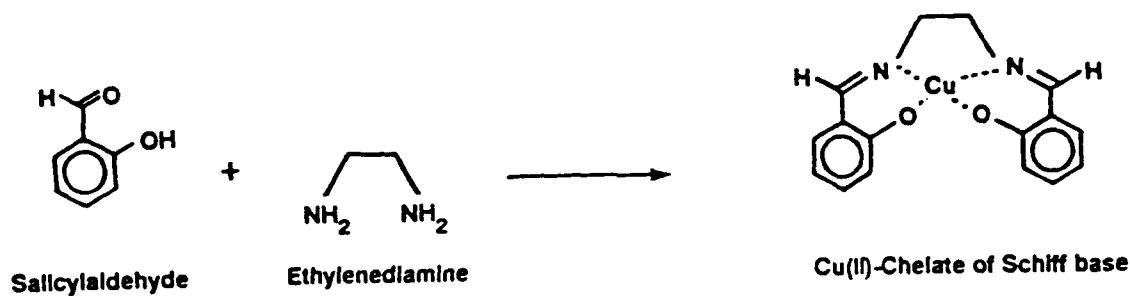
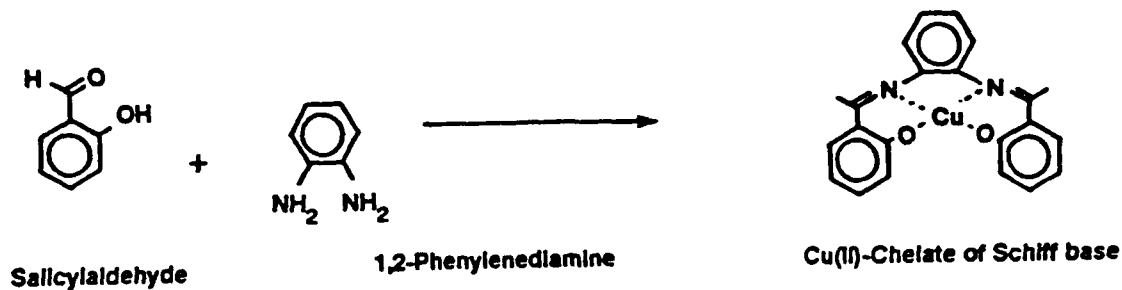
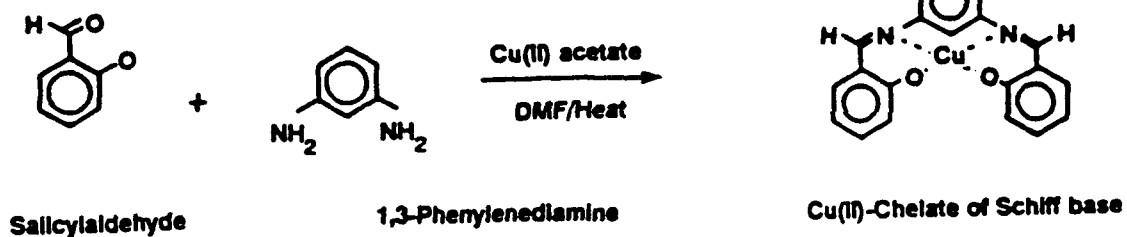


Figure 8. Formation of different schiff base compounds (Continued).

### 2.3.1 Infrared Spectral Method

We have chosen to utilize Fourier Transform Infrared (FTIR) as it provides us the versatility of using small sample size and the capabilities of a microprocessor-controlled instrument. For this program a Nicolet instrument connected to a HP printer, Model 1020 was used. The procedure to confirm the structure of the product, rests on comparing the functional group IR frequency data of the starting compound salicylaldehyde and ethylenediamine with those of the IR group frequency of the, product, i.e., Schiff base. In the case of salicylaldehyde the functional group frequencies are: (1) the phenolic hydroxyl, the C-O stretch of the phenol ( $1365\text{ cm}^{-1}$ ); (2) the aldehydic C-H stretch ( $2900\text{--}2700\text{ cm}^{-1}$ ); and (3) the carbonyl absorption, (C=O)  $1695 \pm 10\text{ cm}^{-1}$  and the  $\text{NH}_2$  group frequency of the ethylenediamine  $3300\text{--}3000\text{ cm}^{-1}$ . In the Schiff base, the structural features in general will show the presence of the C=N 'Imine' ( $1616 \pm 25\text{ cm}^{-1}$ ) and the C-O of the phenolic groups and the absence of (i) the carbonyl group, (ii) the aldehydic hydrogen, and (iii) the free amino group of ethylenediamine. Salicylaldehyde shows the characteristic IR absorption from  $3000\text{ to }3300\text{ cm}^{-1}$  for the phenolic hydroxyl,  $2700\text{ and }2900\text{ cm}^{-1}$  for the aldehydic hydrogen (H-C=O) and the carbonyl frequency at  $1695\text{ cm}^{-1}$ . In addition, the aromatic stretch frequencies are seen from  $1500\text{ cm}^{-1}$  to  $1300\text{ cm}^{-1}$ .

In the Schiff base obtained by the reaction of the above two compounds in warm ethanol at  $60^\circ\text{C}$  the IR spectrum shows a strong peak at  $1616\text{ cm}^{-1}$ . Literature group frequency identifies this peak with the presence of the imine functionality (C=N) in the molecule. The Schiff base also exhibits a peak at  $1379\text{ cm}^{-1}$  for the phenolic C-O bond. The proof of the formation is further substantiated by the absence of: (1) aldehydic protons (H-C=O) at  $2700/2900\text{ cm}^{-1}$ ; and (2) the aldehydic carbonyl group at  $1695\text{ cm}^{-1}$ . Using the above rationale, the IR spectral data of all the compounds listed in Table 1 have been examined, and the formation or otherwise of the proposed Schiff bases has been confirmed.

Our method of elucidating the structure(s) of the candidate will be demonstrated in some detail for the Schiff base compound derived from salicylaldehyde and ethylenediamine.

Structures of the compounds are elucidated by IR utilizing known group frequencies and absorption intensity profiles. IR spectra reported in this study are in inverse centimeters or  $\text{cm}^{-1}$ . Samples are scanned in the spectral range  $400\text{ cm}^{-1}$  to  $4,000\text{ cm}^{-1}$  and the functional group positions are reported in  $\text{cm}^{-1}$ . In order to scan a sample by IR, KBr pellets of the samples are prepared and used. A KBr pellet of the sample is prepared by intimately grinding anhydrous KBr with the test compound and compressing the KBr-test mixture in a die at high pressures. A clear transparent disc is required to obtain a good IR scan. Most often the ratio of KBr to organic compound is anywhere between 90% KBr and 10% organic test component to 99% KBr and 1% organic test component. The disc is then placed in a cell holder and introduced into the path of the infrared radiation of the IR instrument. The sample is scanned in the range  $400\text{ cm}^{-1}$  to  $4,000\text{ cm}^{-1}$  initially in order to establish regions in the spectrum where intense absorptions occur. Next the sample is scanned again in the region of intense absorptions. This is done so as to be able to properly identify the functional groups present in the compound and utilize these absorption peaks to confirm the structures. The spectral peaks of all the compounds investigated are tabulated in Table 6. They include IR data of the compounds prior to heating at  $200^{\circ}\text{C}$  and after heating at  $200^{\circ}\text{C}$  for 48 hours.

### 2.3.2 Nuclear Magnetic Resonance Method (NMR)

In an NMR method of characterization of organic compounds, structure is elucidated by the appearance of different protons in different radio frequency resonance ranges. The different hydrogens appear at different resonance regions depending on the shielding or deshielding of the proton (under consideration) by the neighboring centers. The NMR data are integrated in order to obtain the number of protons of a given type. Over all, protons are identified by: (1) position of the NMR spectral peak which is reported in parts per million (ppm); (2) the multiplicity of the given proton which arises due to coupling with adjacent protons; and (3) integration which provides information on the sum total of the protons present in the molecule. NMR provides an added advantage, i.e., it is used to determine the purity of the compound by the occurrence or non-occurrence of peaks in addition to the expected peaks. An NMR experiment is run by dissolving the sample in a deuterated solvent (at least 99.8% incorporation of deuterium). In our case we chose  $d_6$ -DMF along with tetramethylsilane (TMS) as the internal standard. The above solution is



transferred to an NMR tube, the tube is capped and then run in the NMR instrument in the range 0 ppm to +12 ppm. Normally 10 ppm is the upper limit of the scan, but in some instances the scans are extended to +12 ppm to examine enolic protons.

The spectral peak positions are reported in ppm. We have used this technique, when possible, for elucidating the structures of the Schiff Bases synthesized in this research. NMR scans of the starting material(s) and the reaction products (Schiff base) are run. The advantage of the FTNMR are quite similar to those of the FTIR both in terms of sample size and data handling. In addition, as compared to a continuous wave (CW) NMR, the resolution of the spectrum is excellent in FTNMR.

We will outline below the approach for elucidating the structures of the compounds, using as an example the Schiff base compound obtained from salicylaldehyde and ethylenediamine. NMR spectra of the pure starting materials were run first. In the case of salicylaldehyde molecule, the four aromatic protons appear as a very complex multiplet in the range, 6.9 to 7.9 ppm. It integrates for four protons. The aldehydic proton ( $\text{H}-\text{C}=\text{O}$ ) and the phenolic proton ( $\text{H}-\text{O}$ ) appear at 9.0 and 10.3 ppm, respectively and they integrate for a single proton each. In the case of the ethylenediamine molecule, the four protons of  $\text{CH}_2-\text{CH}_2$  and four protons of the two  $\text{NH}_2$  groups appear at 2.8 and 1.2 ppm respectively with appropriate integration values.

The product Schiff base has a characteristic NMR. The phenolic proton ( $-\text{O}-\text{H}$ ) appears at 8.3 ppm and the imine proton ( $\text{H}-\text{C}=\text{N}$ ) at 3.75 ppm which integrates for 1 proton each. This proves that the desired Schiff base has been produced by the reaction and that it is free of any impurities or the starting materials.

In a similar manner the Schiff base that was synthesized from salicylaldehyde and 4,4'-benzidine was examined. Along with the above compound, it is listed in Table 5. IR spectral data are shown in Table 6 and the structural formula in Figure 8.

### 2.3.3 Spectral Analysis

#### 2.3.3.1 Bissalicylaldehyde-4,4'-Benzidine Schiff Base

This compound is referred to as compound B in Table 5. Its overall IR spectral data are summarized in Table 6 and its structural formula is represented in Figure 8. The IR spectra show intense absorption at 1616, 1574, 1496, and 1361  $\text{cm}^{-1}$ . The spectral peak at 1616  $\text{cm}^{-1}$  is associated with the imine functional group indicating that the Schiff base bissalicylaldehyde-4,4'-benzidine has been formed. Further proof of its formation is the absorption peak at 1361  $\text{cm}^{-1}$  which is associated with the C-O band of the phenol group. In addition, the presence of aromatic stretching bands at 1574 and 1496  $\text{cm}^{-1}$  lend support to the correct structural deduction of the Schiff base. The absence of any carbonyl absorption (1695  $\text{cm}^{-1}$ ) and amino group absorption (3,300-3,000  $\text{cm}^{-1}$ ) provide evidence that the compound is free of contamination by any of the starting materials.

#### 2.3.3.2 Schiff Base Derived From Salicylaldehyde and 1,2-Phenylenediamine

The reference number of this compound in Table 5 is (D). The consolidated IR data are shown in Table 6 and the structural formula in Figure 8. The compound shows IR absorption peaks at 1616, 1556, 1371, and 761  $\text{cm}^{-1}$ . The peak at 1616  $\text{cm}^{-1}$  and 1371  $\text{cm}^{-1}$  have been identified to represent the imine group and the C-O bond of phenols. The peaks at 1556  $\text{cm}^{-1}$  and 761  $\text{cm}^{-1}$  represent the C-H stretching frequency and the presence of  $\bar{o}$  substituted benzene ring respectively. These data support the formation of bissalicylaldehyde-1,2-phenylenediimine compound. The absence of both the carbonyl absorption band at 1695  $\text{cm}^{-1}$  and 3300-3000  $\text{cm}^{-1}$  band for amino group indicates that a pure Schiff base has been isolated.

#### 2.3.3.3 Schiff Base Derived From Acetylacetone and Ethylenediamine

This compound referred by (c) in Table 5. The IR data of this compound are shown in Table 6 and structural formula in Figure 8. The compound exhibits IR absorption at 1614, 1369  $\text{cm}^{-1}$ . The absorption at 1614  $\text{cm}^{-1}$  is identified with the imine functional group (C=N) and the absorption peak at 1369 with the C-O bond. The presence of these two functional group absorptions, the absence of carbonyl and amino group absorptions prove that a pure sample of bisacetylacetoneethylenediimine Schiff base has been formed.

**2.3.3.4 Copper Chelate of Schiff Base Derived From Bissalicylaldehyde-4,4'-Benzidine**

This compound is identified by (H) in Table 5. The consolidated IR data are shown in Table 6 and structural formula in Figure 8. Its IR absorption peaks appear at 1607 and 1379  $\text{cm}^{-1}$ . Both these absorption frequencies indicate the presence of the imine and phenolic C-O groups respectively. No hydroxyl group peaks in the region 3650-3300  $\text{cm}^{-1}$  are seen in the spectra. This indicates that the phenolic hydroxyl is absent. The formation of the copper chelate of the Schiff base is thus indicated.

**2.3.3.5 Schiff Base Derived From Salicylaldehyde and 1,3-Phenylenediamine**

This compound is identified by (M) in Tables 5 and 6. Its structural formula is shown in Figure 8. The 1616  $\text{cm}^{-1}$  IR absorption peak is present in the product substantiating the formation of the Schiff base. Further, there are the usual bands for  $\bar{o}$  substituted aromatic ring at 754 and 753  $\text{cm}^{-1}$ . The sample is pure as proved by the absence of any IR peaks characteristic of the starting materials. The NMR spectrum of the product shows the presence of the phenolic hydroxyl proton (8.3 ppm, 1H) and the aromatic ring protons as a complex multiplet (6.9-7.9 ppm). Based on these spectral data it is concluded that the product isolated is the Schiff base, i.e., bissalicylaldehyde 1,3-phenylenediimine.

**2.3.3.6 Schiff Base of 1,3-Phenylenediamine and Acetylacetone**

This compound is referred to as (N) in Table 5. The consolidated IR data are shown in Table 6 and the structural formula in Figure 8. The spectral data show an absorption peak at 1664  $\text{cm}^{-1}$ . Although it is on the shorter frequency range, literature reports support it to be due to the imine functional group. The absence of carbonyl absorption (1700-1735  $\text{cm}^{-1}$ ) and the peak due to the amino group (3300-3000  $\text{cm}^{-1}$ ) show that a pure Schiff base has been obtained.

**2.3.3.7 Schiff Base of Acetylacetone With 1,2-Phenylenediamine**

Table 5 lists this compound under the identification (O). The IR data are shown in Table 6 and the structural formula in Figure 8. The spectral

data show absorption peaks at 1632, 1370, 764  $\text{cm}^{-1}$ . The peak at 1632  $\text{cm}^{-1}$  has been identified with the imine functional group. The C-O for the alcohol or hydroxyl group and the 764  $\text{cm}^{-1}$  for an o<sup>-</sup> substituted benzene ring, i.e., in this case the 1,2-phenylenediamine. On the basis of these data it can be stated that the bisacetylacetone 1,2-phenylenediimine Schiff base has been obtained in a pure form.

#### 2.3.3.8 Schiff Base of Salicylaldehyde With 1,2-Phenylenediamine

The compound is identified by (D) in Table 5. The IR spectral data are shown in Table 6 and structural formula in Figure 8. The sample shows intense IR absorption peaks at 1616; 1371, 761  $\text{cm}^{-1}$ . The peak at 1616  $\text{cm}^{-1}$  represents the imine group (C=N), at 1371  $\text{cm}^{-1}$ , the phenolic (C-O) bond and at 761  $\text{cm}^{-1}$  that of o<sup>-</sup>-substituted benzene ring. No absorption peaks characterizing the starting material peaks [1695  $\text{cm}^{-1}$  (C=O), 3500  $\text{cm}^{-1}$  (-NH<sub>2</sub>)] are observed in the spectra of the product, indicating that the product isolated is a pure compound.

#### 2.3.3.9 Cu(II) Chelate of Bissalicylaldehydeethylenediimine

In Table 5, this compound is listed as (E). The IR spectral data are shown in Table 6 and the structural formula in Figure 8. The compound shows an absorption at 1647  $\text{cm}^{-1}$  representing the imine group (C=N) and 1331  $\text{cm}^{-1}$  for the phenolic C-O. These data indicate that the desired chelate has been obtained.

#### 2.3.3.10 Cu(II) Chelate of Schiff Base Derived From Salicylaldehyde and 4,4'-Benzidine

The IR spectra obtained by using KBr disc of the compound shows peaks at 1607  $\text{cm}^{-1}$  (C=N), 1379  $\text{cm}^{-1}$  (C-O), and 770-730 (o<sup>-</sup>-disubstituted aromatic) indicating the formation of the desired product (Table 6).

#### 2.3.3.11 Cu(II) Chelate of Schiff Base Derived From Salicylaldehyde and 1,2-phenylenediamine

The IR spectra data shown in Table 6, i.e., 1620 (C=N) (imine group), 1378, (C-O) (phenolic stretch) 733 (o<sup>-</sup>-substituted benzene ring) confirm the formation of the chelate (see Table 6).

2.3.3.12 Cu(II) Chelate of Schiff Base Derived From Salicylaldehyde and 1,3-Phenylenediamine

Table 6 shows the IR spectral data obtained for this compound. The peaks at  $1605\text{ cm}^{-1}$  (C=N imine),  $1379\text{ cm}^{-1}$  (C-O, phenolic),  $756\text{ cm}^{-1}$  (o-substituted benzene ring) confirm the formation of the chelate as the product (Table 6).

2.3.3.13 Cu(II) Chelate of Schiff Base Derived From Acetylacetone and Ethylenediamine

The presence of IR spectral peaks at  $1581\text{ cm}^{-1}$  (C=N, imine),  $1354\text{ cm}^{-1}$  (c-o-alcoholic) confirm the formation of the chelate as the product (see Table 6).

2.3.3.14 Cu(II) Chelate of Acetylacetone-1,2-Phenylenediimine

The IR spectra of the product (Table 4) at  $1570\text{ cm}^{-1}$  (C=N imine),  $1398\text{ cm}^{-1}$  (C-O of hydroxyl) confirms the formation of the Schiff base chelate (see Table 6).

2.3.3.15 Cu(II) Chelate of Acetylacetone-1,3-Phenylenediimine

The formation of the Schiff base chelate in the product is strongly indicated by the IR-spectral peaks at  $1576\text{ cm}^{-1}$  (C=N, imine) and  $1352\text{ cm}^{-1}$  (C-O of hydroxyl group) (Table 6).

## 2.4 THERMAL STABILITY OF THE CANDIDATE COMPOUNDS

### 2.4.1 Thermo-Oxidation Testing

One of the main objectives of the program is to screen and select compounds that could be used as additives or as lubricants themselves at temperatures of up to  $200^{\circ}\text{C}$ . Thermo-oxidation tests were therefore carried out in the program in order to determine the thermal stability of the compounds. Briefly, samples were exposed in a box furnace to slowly flowing air ( $<5\text{ SCFH}$ ) at a temperature of  $200^{\circ}\text{C}$  for varying periods of time. Any compound that lost 30% or more in weight after a given time interval (i.e., 16 hr) was removed from the test and was considered not to be thermally stable.

In addition to the candidate compounds (both the free ligand and Cu(II) chelates of the ligands) synthesized in this program a few commercially available (off-the shelf) compounds were selected for this study. These are phthalocyanine, copper phthalocyanine, mesotetraphenyl porphyrin and hemato-

**Contract No. N62269-88-R-0234**  
**Report No. NADC-91049-60**

porphyrin. Of these only the first-three commercially available compounds were used. The four phenyl rings in mesotetraphenyl porphyrin being planar, in our view, would provide a larger surface area coverage and also be thermally more stable. In addition, all the candidate compounds have been chosen with the objective of square planar geometry for the chelates and overall planarity of the molecule.

In this segment of the study, stability tests were carried out with the objective of screening and eliminating those compounds which are not thermally stable and thus select the candidate compounds possessing appropriate thermal properties. For the thermal stability tests, a furnace was secured which was capable of accommodating about 100 porcelain crucibles of 15 mL capacity each. The furnace was maintained at 200°C and had arrangements for flow of air through it. The main objective of this was to determine the loss in weight of the sample as a result of heating at the given temperature over the test period and to examine structural changes, if any. Known quantities of the pure candidate compounds were weighed into the crucibles and introduced into the furnace maintained at 200°C. At the end of 16 hours under the above experimental conditions, samples were withdrawn and weighed. Those samples which lost weight greater than 25% of their starting weight were removed from the thermal studies. This was done based on the idea that further thermal treatment would only lead to greater weight loss and not provide any useful insight on the compound.

Those samples which did not suffer appreciable weight loss were continued to be heated in the furnace for a total of 48 hours and once more weighed, and based on weight loss (as earlier) samples were rejected. Another criterion for the rejection of samples for continued thermal studies is based on the differential thermal weight loss. Data on the differential weight loss are shown on Table 7. It should be noted that after 48 hours of heating there is very little change in differential weight loss in a few cases. As a result of the testing of an initial list of 18 compounds, seven compounds proved to be "thermally stable" (i.e., upon heating at 200°C for 1,000 hours) and these are listed below: Schiff bases from (1) salicylaldehyde and ethylenediamine (2) salicylaldehyde and 1,3-phenylenediamine (3) Cu(II) chelates of samples (1) and (2) and finally the off-the-shelf (commercially available) compounds i.e., (3) phthalocyanine (4) copper phthalocyanine and (5) mesotetraphenylporphyrin, (see Table 8). These are structurally represented in Figures 9 and 10.

TABLE 7. THERMAL AND OXIDATIVE (AIR) STABILITY OF CANDIDATE COMPOUNDS

| Sample Identification | Reference in Log Book      | Weight loss due to Heating at 200°C in Air |       |      |       |        | Differential Loss, % |        |          | Chemical Description                                   |
|-----------------------|----------------------------|--|-------|------|-------|--------|----------------------|--------|----------|--|
|                       |                            | Average Total Loss, %                      | 16 h  | 48 h | 250 h | 1000 h | 16/48                | 48/250 | 250/1000 |  |
| A                     | ** C6687-1                 | 3.5%                                       | 17.0% | 0.0% | 0.0%  | 0.0%   | 13.5%                | 0.0%   | 0.0%     | Salicylaldehyde + Ethylenediamine                      |
| B                     | ** C6687-3                 | 1.1%                                       | 9.2   | 0.0% | 0.0%  | 0.0%   | 8.1%                 | 0.0%   | 0.0%     | Salicylaldehyde + Benzidine                            |
| C                     | ** C6687-4                 | 36.5%                                      | 74.7% | 0.0% | 0.0%  | 0.0%   | 38.2%                | 0.0%   | 0.0%     | Acetylacetone + Ethylenediamine                        |
| D                     | ** C6687-5                 | 2.0%                                       | 32.8% | 0.0% | 0.0%  | 0.0%   | 30.8%                | 0.0%   | 0.0%     | Salicylaldehyde + 1,2-Phenylenediamine                 |
| E                     | ** C6687-11                | 26.2%                                      | 24.7% | 0.0% | 0.0%  | 0.0%   | -1.5%                | 0.0%   | 0.0%     | Cu Chelate from (A)                                    |
| F                     | ** C6687-12                | 2.4%                                       | 40.6% | 0.0% | 0.0%  | 0.0%   | 38.2%                | 0.0%   | 0.0%     | Cu Chelate from (D)                                    |
| G                     | ** C6687-13                | 2.5%                                       | 1.4%  | 0.0% | 0.0%  | 0.0%   | -1.1%                | 0.0%   | 0.0%     | Cu Chelate from Salicylaldehyde + 1,3-Phenylenediamine |
| H                     | ** C6687-14                | 1.4%                                       | 63.2% | 0.0% | 0.0%  | 0.0%   | 61.8%                | 0.0%   | 0.0%     | Cu Chelate from (B)                                    |
| I                     | ** C6687-15                | 7.4%                                       | 15.7% | 0.0% | 0.0%  | 0.0%   | 8.3%                 | 0.0%   | 0.0%     | Cu Chelate from (C)                                    |
| J                     | ** C6687-16                | 28.3%                                      | 34.6% | 0.0% | 0.0%  | 0.0%   | 6.4%                 | 0.0%   | 0.0%     | Cu Chelate from Acetylacetone + 1,2-Phenylenediamine   |
| K                     | ** C6687-17                | 73.8%                                      | 72.9% | 0.0% | 0.0%  | 0.0%   | -0.1%                | 0.0%   | 0.0%     | Cu Chelate from Acetylacetone + 1,3-Phenylenediamine   |
| L                     | ** C6687-18                | 74.3%                                      | 74.1% | 0.0% | 0.0%  | 0.0%   | -0.3%                | 0.0%   | 0.0%     | Cu Chelate from Acetylacetone + Benzidine              |
| M                     | ** C6687-19                | 5.0%                                       | 7.0%  | 0.0% | 0.0%  | 0.0%   | 2.0%                 | 0.0%   | 0.0%     | Salicylaldehyde + 1,3-Phenylenediamine - Schiff Base   |
| N                     | ** C6687-20                | 44.6%                                      | 43.3% | 0.0% | 0.0%  | 0.0%   | -1.3%                | 0.0%   | 0.0%     | Acetylacetone + 1,3-Phenylenediamine - Schiff Base     |
| O                     | ** C6687-21                | 76.3%                                      | 75.7% | 0.0% | 0.0%  | 0.0%   | -0.6%                | 0.0%   | 0.0%     | Acetylacetone + 1,2-Phenylenediamine - Schiff Base     |
| P                     | Phthalocyanine (Kodak)     | 0.4%                                       | 0.2%  | 0.0% | 0.0%  | 0.0%   | -0.2%                | 0.0%   | 0.0%     | Phthalocyanine (Kodak)                                 |
| Q                     | Phthalocyanine (Kodak)     | 1.5%                                       | 5.1%  | 0.0% | 0.0%  | 0.0%   | 3.6%                 | 0.0%   | 0.0%     | Phthalocyanine (Cu)                                    |
| R                     | Mesotetraphenyl Porphyrine | 0.4%                                       | 0.3%  | 0.0% | 0.0%  | 0.0%   | 0.0%                 | 0.0%   | 0.0%     | Mesotetraphenyl Porphyrine                             |

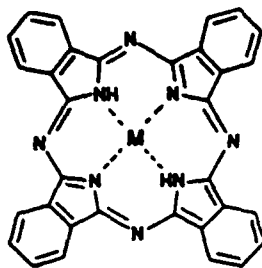
V - MIL-G-10924E No additives - 1.6%, 3.4%, 12.2%, 17.0%.  
W - MIL-G-10924E with additives - 2.5%, 4.0%, 8.4%, 26.5%

TABLE 8. LIST OF "THERMALLY STABLE" CANDIDATE COMPOUNDS

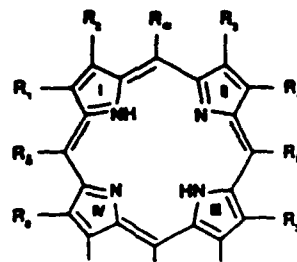
| Sample Identification | Chemical Description  |
|-----------------------|---|
| A                     | Schiff base from salicylaldehyde and ethylenediamine        |
| B                     | Schiff base from salicylaldehyde and benzidine              |
| M                     | Schiff base from salicylaldehyde and 1,3-phenylenediamine   |
| E                     | Cu (II) chelate of bis-salicylaldehydeethylenediamine       |
| G                     | Cu (II) chelate of bis-salicylaldehyde 1,3-phenylenediamine |
| P                     | Phthalocyanine  |
| Q                     | Copper (II) phthalocyanine                                  |
| R                     | Mesotetraphenyl porphyrin                                   |

These candidate compounds have exhibited thermal stability based on weight loss characteristics upon heating for 1,000 hours at 200°C in air.

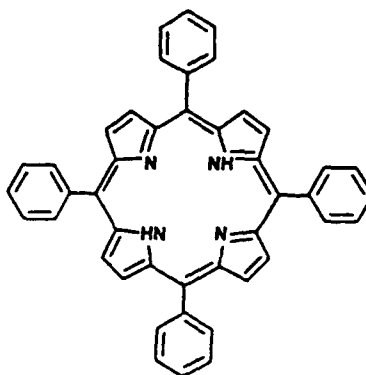




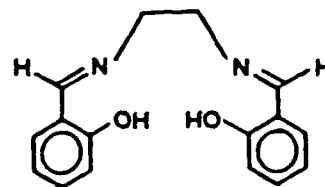
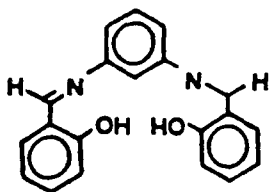
PHthalocyanine (M=H)  
COPPER PHthalocyanine (M=Cu)



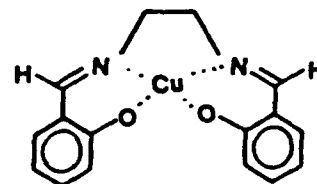
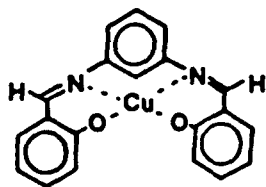
PORPHYRIN STRUCTURE WITH THE SUBSTITUENT POSITIONS



MESOTETRAPHENYL PORPHYRIN

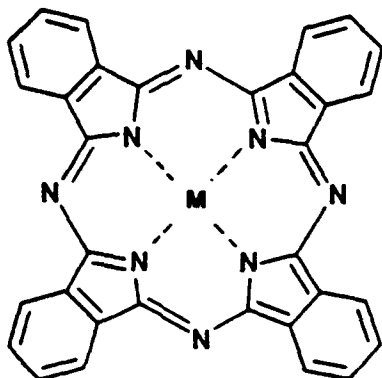


SCHIFF BASE

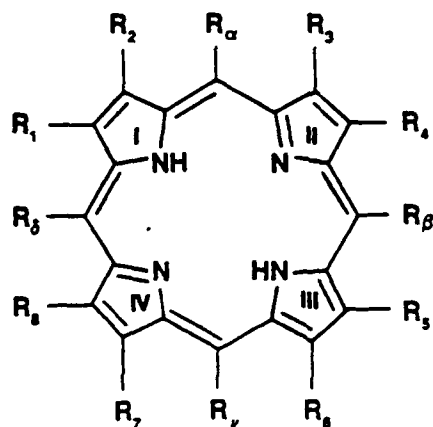


COPPER CHELATES OF SCHIFF BASES

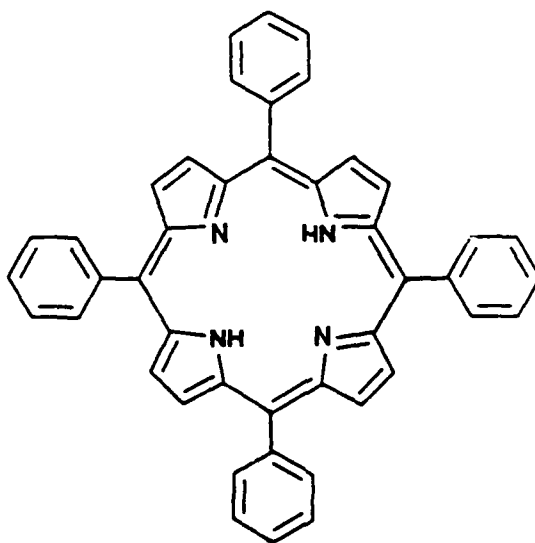
Figure 9. Thermally stable compounds selected for this research.



PHthalOCYANINE (M=H)  
COPPER PHthalOCYANINE (M=Cu)



PORPHYRIN STRUCTURE WITH THE SUBSTITUENT POSITIONS



MESOTETRAPHENYL PORPHYRIN

Figure 10. Off-the-shelf (commercial) compounds used in this research.

Prior to discontinuation of thermal studies of the samples, each sample was subjected to examination by infrared spectral method.

All the Schiff Base samples were scanned by IR spectral method after thermal testing, in order to determine the changes before and after thermal treatment. These are shown in Table 6. Those samples which survived the 48 hours of thermal treatment, were subjected to 250 and 1000 hours of thermal treatment. Data presented in Table 8 indicate that after 48 hours there was very little direct or differential loss in weight.

Having narrowed the number of candidate compounds from 18 to 7 based on the above thermal treatment for 1,000 hours, the desired Schiff bases and their Cu(II) chelates were prepared in 20-40 gram lots.

#### 2.4.2 Differential Scanning Calorimetric (DSC) Analysis of Selected Schiff Bases and Their Cu<sup>+2</sup> Chelates

Among the compounds selected for investigation in this program, eight compounds were found to be suitable for lubricant formulation study on the basis of thermo-oxidation tests over a 1,000 hour period (see Table 8). These eight compounds were subjected to DSC analysis. The experiments carried out in this series and the results obtained are presented here.

Four Schiff bases and their corresponding Cu<sup>+2</sup> chelates were analyzed by Differential Scanning Calorimetry (DSC). The analysis was undertaken to ascertain the thermal oxidation resistance of the chelates relative to their corresponding Schiff bases and to ascertain the order of stability within this set of compounds. These eight compounds and their corresponding SAMPLE CODE numbers are listed in Tables 9A and 9B. Each material is identified by its COMPOUND NUMBER in Table 10. Odd compound numbers identify Schiff base materials, and even compound numbers, the respective Cu<sup>+2</sup> chelates.

DSC, a thermal analysis procedure, is a refinement of Differential Thermal Analysis. In the DSC procedure a sample cell and reference cell are enclosed in close proximity to each other and share a common thermal environment. The average temperature of the combined cells is heated at a fixed rate (deg.C/min), and the temperature difference between the sample cell containing a test material and the reference cell containing a suitable reference material is monitored. When the sample experiences an endothermic process, it

TABLE 9A. MATERIALS ANALYZED BY DSC

| Compound No. | Compound   |
|--------------|--|
| 1            | Bis-Salicylaldehydeethylenediimine-Schiff Base                             |
| 2            | Bis-Salicylaldehydeethylenediimine-Schiff Base-Cu <sup>+2</sup> Chelate    |
| 3            | Bis-Salicylaldehyde-1,3-phenylenediimine-Schiff Base                       |
| 4            | Salicylaldehyde-1,3-phenylenediimine-Schiff Base, Cu <sup>+2</sup> Chelate |
| 5            | Salicylaldehyde-4,4'-benzidine-Schiff Base                                 |
| 6            | Salicylaldehyde-4,4'-benzidine-Schiff Base, Cu <sup>+2</sup> Chelate       |
| 7            | Phthalocyanine   |
| 8            | Cu <sup>+2</sup> - Phthalocyanine Chelate                                  |

TABLE 9B. TEST SAMPLE DESIGNATIONS

| Compound No. | Sample Code             |                         |                    |
|--------------|-------------------------|-------------------------|--------------------|
|              | Sealed Pan Nitrogen ATM | Vented Pan Nitrogen ATM | Vented Pan Air ATM |
| 1            | 11-01                   | 11-02                   | 11-03              |
| 2            | 12-01                   | 12-02                   | 12-03              |
| 3            | 13-01                   | 13-02                   | 13-03              |
| 4            | 14-01                   | 14-02                   | 14-03              |
| 5            | 15-01                   | 15-02                   | 15-03              |
| 6            | 16-01                   | 16-02                   | 16-03              |
| 7            | 17-01                   | 17-02                   | 17-03              |
| 8            | 18-01                   | 18-02                   | 18-03              |

**Contract No. N62269-88-R-0234**  
**Report No. NADC-91049-60**

**TABLE 10. DSC SAMPLE WEIGHT LOSSES**

| Compound<br>No. | WT% (Tmax, deg.C)       |                         |                        | DSC<br>Exotherm<br>Vented Pan<br>Air ATM | Melting<br>Point<br>(deg.C) |
|-----------------|-------------------------|-------------------------|------------------------|--|-----------------------------|
|                 | Sealed Pan<br>N2 ATM    | Vented Pan<br>N2 ATM    | Vented Pan<br>Air ATM  |  |                             |
| 1               | 11.5 (320)              | 53.7 (320)              | 69.9 (340)             | #  | 123                         |
| 2               | 18.7 (340)<br>0.5 (320) | 40.9 (350)<br>0.4 (320) | 21.5 (340)             | ###                                      |                             |
| 3               | 21.5 (340)              | 23.7 (340)              | 36.9 (350)             | #  | 105                         |
| 4               | 0.6 (350)-02 (340)      |                         | 13.7 (350)             | ###                                      |                             |
| 5               | -0.1 (320)              | -0.3 (345)              | 3.0 (350)              | #  | 264                         |
| 6               | 14.1 (380)<br>6.3 (320) | 6.0 (320)               | 8.2 (320)<br>5.4 (320) | ###<br>###                               |                             |
| 7               | 0.3 (380)               | 0.6 (380)               | 0.2 (340)              | #  |                             |
| 8               | 0.4 (340)<br>0.7 (345)  | 2.5 (340)<br>3.6 (345)  | 2.3 (340)<br>2.4 (340) | #<br>#                                   |                             |

# : Small exotherm observed in DSC run under atmosphere of air

###: Large exotherm observed in DSC run under atmosphere of air

\* : Measured wt losses <=0.5% are in the noise of the measurements

will tend to lag in temperature relative to the reference material temperature. When it undergoes an exothermic process, it will give off heat and, therefore, will tend to lead the reference material temperature. Special independent heaters have been built into each of the two cells. Heat to the sample cell is increased or decreased relative to the reference cell in order to maintain an overall fixed heating rate (deg.C) of the system. The current to the heater is directly related to the power (joules/sec) needed to maintain the constant heating rate. This current level is translated into voltage and recorded on a millivolt strip chart recorder. Departures in the DSC outputs from baseline levels are then interpreted in terms of endothermic and exothermic activity of the test compound.

For these analyses, a Perkin-Elmer DSC-1B was used. The instrument has a temperature range of -100 to +500 deg.C and uses samples up to a maximum size of 0.05 mL in volume ( $\leq 100$  mg at a density of 2 g/mL) in each crimp sealed disposable pan. Scan rates of 0.625 to 80 deg.C are selectable in eight fixed steps. A full-scale ordinate range of 1 to 32 mcal/sec is available in six fixed steps and the ultimate noise level of the instrument is 40 microcal/sec.

In our present analyses, sample sizes from 1 to 5 mg were used. Runs were started at 40 deg.C and recorded to at least 320 deg.C. All of the included thermograms in the corresponding figures were conducted at a range of 16 mcal/sec and a scan Speed of 10 deg.C/min. The recorder was set at a Recorder Range of 10 mv full scale and Chart Speed of 10 mm/min.

Three separate analyses were conducted for each of the eight materials: (i) sample in crimp-sealed pan under High Purity (HP) nitrogen atmosphere (constantly flowing through the DSC head at 20 ml/min.); (ii) sample in a vented top pan under HP nitrogen atmosphere; and (iii) sample in a vented top pan under Zero air. Thermograms of sealed and vented samples under nitrogen were compared to identify endotherms associated with evaporation or sublimation of a material. Thermograms of samples exposed to air were compared to the same material run under nitrogen to ascertain exothermic behavior associated with oxidation. In lieu of doing thermogravimetric Analysis, samples were weighed before and after each DSC run and the weight losses were used to clarify interpretation of the DSC thermograms. These weight losses have been tabulated in Table 11 as WT% of the initial material. Sample weights of 1 to

**Contract No. N62269-88-R-0234**  
**Report No. NADC-91049-60**

**TABLE 11. DSC SAMPLE WEIGHT LOSSES AT 200°C**

| Sample No. | DSC ATM | DSC PAN | Wt% (Tmax, deg.C) |      |              | Melting Point (deg.C) |
|------------|---------|---------|-------------------|------|--------------|-----------------------|
|            |         |         | 200C              | 320C | Other [Tmax] |                       |
| 1          | N2      | Sealed  | 1.8               | 11.5 |              | 123                   |
|            | N2      | Vented  | 0.7               | 53.7 |              |                       |
|            | Air     | Vented  | 0.6               |      | 69.9 [340]   |                       |
| 2          | N2      | Sealed  | 0.1               | 0.5  | 18.7 [340]   | *                     |
|            | N2      | Vented  | 0.2               | 0.4  | 40.9 [350]   |                       |
|            | Air     | Vented  | 0.4               |      | 21.5 [340]   |                       |
| 3          | N2      | Sealed  | 0.0               |      | 21.5 [340]   | 105                   |
|            | N2      | Vented  | 0.6               |      | 23.7 [340]   |                       |
|            | Air     | Vented  | 0.5               |      | 36.9 [350]   |                       |
| 4          | N2      | Sealed  | -0.1              |      | 0.6 [350]    | *                     |
|            | N2      | Vented  | 2.6               |      | -0.2 [340]   |                       |
|            | Air     | Vented  | 2.8               |      | 13.7 [350]   |                       |
| 5          | N2      | Sealed  | 0.2               | -0.1 |              | 264                   |
|            | N2      | Vented  | 1.5               |      | -0.3 [345]   |                       |
|            | Air     | Vented  | 0.6               |      | 3 [350]      |                       |
| 6          | N2      | Sealed  | 0.3               | 6.3  | 14.1 [380]   | *                     |
|            | N2      | Vented  | 4.4               | 6.0  |              |                       |
|            | Air     | Vented  | 3.6               | 5.4  |              |                       |
| 7          | N2      | Sealed  | 0.5               |      | 0.3 [380]    | *                     |
|            | N2      | Vented  | 0.8               |      | 0.6 [380]    |                       |
|            | Air     | Vented  | 0.6               |      | 0.2 [340]    |                       |
| 8          | N2      | Sealed  | 0.7               |      | 0.4 [340]    | *                     |
|            | N2      | Vented  | 0.8               |      | 2.5 [340]    |                       |
|            | Air     | Vented  | 1.1               |      | 2.4 [340]    |                       |

\*No clear melting points were observed; the compounds showed signs of decomposition.

5 mg were used and weight losses of  $-1/-0.5\%$  may be considered to be in the noise of the measurement. These weight losses are not entirely comparable since the final temperatures, to which the weight changes are most sensitive, were  $>320$  deg.C but not all the same. However, useful comparisons are still evident.

Weight loss measurements were repeated for all the eight compounds at  $200^{\circ}\text{C}$ , since this is the temperature at which the lubricant formulations containing these candidate compounds were tested for their wear- and corrosion resistance characteristics (see Table 11).

The DSC thermogram are given in Figures 1 through 24 (see Appendix 1) and the associated weight changes are summarized in Table 11. The results of the individual DSC thermograms are highlighted below in Table 12.

In general the overall stability of materials in order of increasing stability is:

$$1 < 2, 3 < 6 < 4 < 5, 8 < 7$$

The unchelated materials in order of increasing stability is

$$1 < 3 < 5 < 7$$

while the chelated materials in order of increasing stability is:

$$2 < 6 < 4 < 8$$

The DSC analysis shows that, in general, all of these materials are affected by thermal exposure to an oxidizing atmosphere. However, oxidation of the compound starts only in the vicinity of  $300^{\circ}\text{C}$  ( $270^{\circ}\text{C}$ - $300^{\circ}\text{C}$ ).

Oxidation at the material surface is definitely apparent for samples 4 and 5.

Volatilization is significant for samples 1, 2, 3, and 6, and vapor phase oxidation is suspected to occur for these cases.



TABLE 12. HIGHLIGHTS OF DSC DATA OF CANDIDATE COMPOUNDS

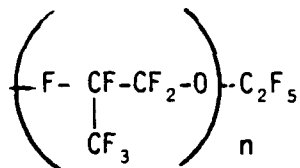
| Sample No. | Observation  |
|------------|--|
| 1 -01      | MP = 123C; slight endotherm and some wt loss observed                                      |
| -02        | Extensive evaporation/decomposition in sample with large wt loss                           |
| -03        | Slight exotherm, very large wt loss may be due to high Tmax (340C)                         |
| 2 -01      | Little wt loss to 320C; no melt  |
| -02        | Negligible wt loss to 320C   |
| -03        | Large exotherm starting 270C, wt loss to 340C similar to wt loss for [2-01] to 340C        |
| 3 -01      | MP = 105C; extensive gradual wt loss   |
| -02        | Ditto  |
| -03        | Slight exotherm over [3-02] baseline   |
| 4 -01      | No wt loss to 350C   |
| -02        | Ditto to 340C  |
| -03        | Large exotherm starting at ~270C; wt loss (350C) attribute to air exposure                 |
| 5 -01      | MP = 264C; no wt loss to 320C  |
| -02        | No wt loss to 345C   |
| -03        | Small exotherm over [5-02] attribute to air exposure (350)                                 |
| 6 -01      | Wt loss to 320C from vaporization and/or decomposition; pan seal burst and vented at ~250C |
| -02        | Ditto; vented pan  |
| -03        | Very large exotherm starting at ~300C may be in gas phase                                  |
| 7 -01      | Very stable to 380C  |
| -02        | Ditto  |
| -03        | Slight exotherm to 340C; no wt loss  |
| 8 -01      | No wt loss to 340C   |
| -02        | Slight wt loss to 340C by venting  |
| -03        | Slight exotherm but no increase in wt loss in air to 340C                                  |

Large exotherms are associated with three of the chelated materials (2, 4, and 6) but not their precursor Schiff bases. This might be due to attack at the  $\text{Cu}^{+2}$  locations.

If the weight losses in these tests were calculated on a molar basis, the effect on the chelated materials would be more than indicated. However, without more laboratory analysis, such detailed examination on the basis of this limited data may not be warranted at this time.

## 2.5 LUBRICANT FORMULATION USING THE CANDIDATE COMPOUNDS

The next step in the investigations was to screen, select, and obtain samples of pure base oils for use in the lubricant formulation. Two types of base oils were identified, i.e., (1) the linear polydimethoxysiloxane polymers from Dow Corning with the following structural feature for the monomer:  $(\text{CH}_3)_3\text{SiO} [\text{SiO} (\text{CH}_3)_2]_n \text{SiMe}_3$  and, (2) Krytox GPL oil. The latter are fluorine end-capped homopolymers of hexafluoroethylene epoxides with the following structure:



manufactured by DuPont. All the base oils are thermally stable at  $200^\circ\text{C}$ , the temperature of our experiment. Polymethylsiloxanes from Dow Corning can be obtained in a range of viscosity. We have elected to use for our current research the sample with a viscosity of 30,000 CSt, as this does not flow readily.

It was decided that the selected (thermally stable) candidate compounds (i.e., seven-samples) would be blended into the pure base oils described above. These lubricant formulations will then be used in two sets of tests consisting of (1) corrosion and (2) lubrication. The corrosive effect of the pure base oils and the effect of the candidate compounds on corrosion, as well as the lubricating properties of the formulations on bearings were examined. All the formulations consisted of 90% pure base oil and 10% of the pure candidate compounds on a w/w basis.

The procedure primarily consisted in grinding the additive compound into a fine powder. The base oil (known weight) was taken in a beaker and heated to 150°C to increase the fluidity, thereby also aiding dispersion of the additive. The oil was stirred using a high speed stirrer. The powdered solid was then added, in small quantities, to the above rapidly-stirred pure oil maintained at 150°C so as to obtain an uniformly blended sample. Stirring was maintained till the contents attained room temperature and 15 more minutes thereafter. This procedure gave the lubricant formulations listed in Table 13.

#### 2.5.1 Thermo-Oxidation of Grease Formulations

The second series of thermo-oxidation tests consisted of exposing grease formulations made by mixing high temperature base oils with the most stable "lubricant additives" found from earlier tests on the base compounds. In this series, two base oils and two standard greases, i.e., MIL-G-10924E and MIL-G-10924E with additive were included.

The procedure used for the thermooxidation tests of the lubricant formulations was as follows:

1. Filled a clean and dry preweighed crucible with the test sample (i.e., base compound or grease formulation); there were six replicates for each sample;
2. recorded the weight of the crucible with the test sample;
3. exposed the crucible with the sample in a high temperature oven at 200°C for 16 hours;
4. reweighed the cooled crucible with the sample and recorded the value of the weight;
5. placed the crucible with sample back in the furnace and continued heating;
6. repeated steps 4 and 5 at 48, 250, and 1,000 hours;
7. pulled out a grease sample (crucible) at the end of 48 and 1,000 hour interval for its chemical characterization.

Each sample was tested in replicates of six where one of each was pulled out at the end of 16, 48, and 250 hour intervals. The final three crucibles of each sample were removed after 1,000 hour heating. Whenever a weight loss  $\geq 30\%$  occurred, the samples were pulled off from further tests.

TABLE 13. CANDIDATE LUBRICANT FORMULATIONS

| Additive                                    | Dow-Corning-Polysiloxane |                  |                  | DuPont Perfluoro Oil |
|---|--------------------------|------------------|------------------|----------------------|
|   | Viscosity                |                  |                  |                      |
|   | 1,000 cSt                | 10,000 cSt       | 30,000 cSt       |                      |
| 1. Bis-salicylaldehyde Ethylenediamine      | S-C06687-2 (14A)         | S-C06687-2 (14B) | S-C06687-2 (15A) | S-C06687-2 (17A)     |
| 2. Cu Chelate of (1)                        | S-C06687-2 (14C)         | S-C06687-2 (14D) | S-C06687-2 (15B) | S-C06687-2 (17B)     |
| 3. Bis-salicylaldehyde 1,3-Phenylenediamine | -                        | S-C06687-2 (16C) | S-C06687-2 (15F) | S-C06687-2 (17C)     |
| 4. Cu Chelate of (3)                        | -                        | S-C06687-2 (16D) | S-C06687-2 (15G) | S-C06687-2 (17D)     |
| 5. Phthalocyanine                           | S-C06687-2 (14E)         | S-C06687-2 (14F) | S-C06687-2 (15C) | S-C06687-2 (17E)     |
| 6. Cu(II) Phthalocyanine                    | -                        | S-C06687-2 (16A) | S-C06687-2 (15D) | S-C06687-2 (17F)     |
| 7. meso-TetraPhenyl Porphyrine              | -                        | S-C06687-2 (16B) | S-C06687-2 (15E) | S-C06687-2 (17G)     |

Note: Each of the formulation listed above consists of a 10 (w/w) dispersion of the candidate compound(s) in the base oil.

Results of this series of tests on the lubricant formulations are presented in Table 14. Data on the base compounds are also included in this table in order to provide background.

Five among the grease formulations that exhibited the most satisfactory overall performance contained the following base compounds:

- (1) Bissalicylaldehydeethylenediimine
- (2) Copper chelate of 1 above
- (3) Phthalocyanine
- (4) Copper chelate of phthalocyanine
- (5) Mesotetraphenyl Porphyrin

## 2.6 CORROSION TESTING

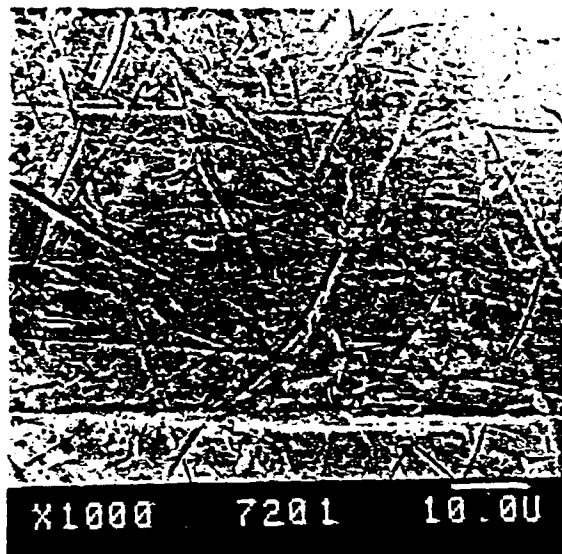
Our work on corrosion testing consisted of exposing specimens of bearing steel (AISI 52100) to the different grease formulations under examination along with samples of the military grease, base oils, and dry condition to serve as standards. The test specimens were cylinder rollers taken from a set of standard bearings. These rollers were placed in sets of three in crucibles and covered and mixed with the test samples of lubricant formulations. The mixture in each crucible was stirred well before exposure to heat to assure complete coverage of the rollers. These crucibles (containing the rollers and lubricants) were then placed in a high temperature oven and exposed at 200°C for varying periods of time. Single sample data were obtained for the corrosion tests at 16, 48, and 250 hour duration and triplicate samples for the 1,000 hour test. Results of the corrosion tests are summarized in Table 15. Data shown in Table 15 indicate that all of the materials under test showed very low corrosion loss for the AISI 52100 bearing steel. This is not unexpected since a 200°C environment does not represent a severe condition for the corrosion of AISI 52100 steel. Selected test specimen (from the corrosion tests) were examined by using optical and/or electron microscopy. Representative photomicrographs are presented here in Figures 11a to 11d. An analysis of all the test steel specimens did not reveal the existence of any corrosion problem in the case of exposure to the IITRI lubricant formulations. In fact, the IITRI formulations exhibit properties that make their use quite attractive for corrosion protection.

TABLE 14. THERMOXIDATION TESTS OF BASE COMPOUNDS AND LUBRICANT FORMULATIONS  
(Test samples exposed to air at 200°C for durations of 16-1000 hrs)

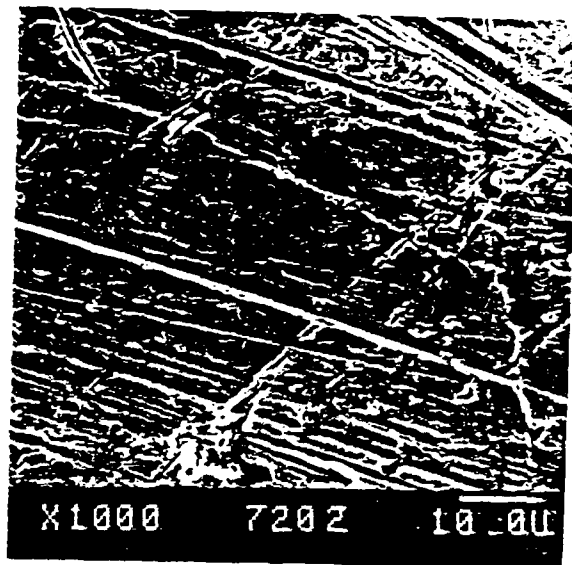
| Sample Code | Compound/Grease  | Average Total Loss, % |       |        |         |       | Differential Loss, % |          |  |
|-------------|--|-----------------------|-------|--------|---------|-------|----------------------|----------|--|
|             |  | 16 hr                 | 48 hr | 250 hr | 1000 hr | 16/48 | 48/250               | 250/1000 |  |
| MIL         | MIL-G-10924E No Additives  | 1.6%                  | 3.9%  | 12.2%  | 17.0%   | 2.3%  | 8.3%                 | 4.8%     |  |
| MIL+        | MIL-G-10924E With Additives  | 2.5%                  | 4.0%  | 8.4%   | 26.5%   | 1.5%  | 4.5%                 | 18.0%    |  |
| A           | Salicylaldehyde + Ethylenediamine                                    | 3.5%                  | 17.0% | 38.4%  | 39.0%   | 13.5% | 21.4%                | 0.6%     |  |
| B           | Salicylaldehyde + Benzidine  | 1.1%                  | 9.2%  | 8.6%   | 11.6%   | 8.1%  | -0.6%                | 3.0%     |  |
| C           | Acetylacetone + Ethylenediamine                                      | 36.5%                 | 74.7% | Pulled | Pulled  | 38.2% | Pulled               | Pulled   |  |
| D           | Salicylaldehyde + 1,2-Phenylenediamine                               | 2.0%                  | 32.8% | Pulled | Pulled  | 30.8% | Pulled               | Pulled   |  |
| E           | Cu Chelate from Salicylaldehyde + Ethylenediamine                    | 26.2%                 | 24.7% | 24.3%  | 35.4%   | -1.5% | -0.4%                | 11.1%    |  |
| F           | Cu Chelate from Salicylaldehyde + 1,2-Phenylenediamine               | 2.4%                  | 40.6% | Pulled | Pulled  | 38.2% | Pulled               | Pulled   |  |
| G           | Cu Chelate from Salicylaldehyde + 1,3-Phenylenediamine               | 2.5%                  | 1.4%  | 2.8%   | 46.1%   | -1.1% | 1.4%                 | 43.3%    |  |
| H           | Cu Chelate from Salicylaldehyde + Benzidine                          | 1.4%                  | 63.2% | Pulled | Pulled  | 61.8% | Pulled               | Pulled   |  |
| I           | Cu Chelate from Acetylacetone + Ethylenediamine                      | 7.4%                  | 15.7% | 46.7%  | Pulled  | 8.3%  | 31.0%                | Pulled   |  |
| J           | Cu Chelate from Acetylacetone + 1,2-Phenylenediamine                 | 28.3%                 | 34.6% | 56.1%  | Pulled  | 6.4%  | 21.4%                | Pulled   |  |
| K           | Cu Chelate from Acetylacetone + 1,3-Phenylenediamine                 | 73.0%                 | 72.9% | Pulled | Pulled  | -0.1% | Pulled               | Pulled   |  |
| L           | Cu Chelate from Acetylacetone + Benzidine                            | 74.3%                 | 74.1% | Pulled | Pulled  | -0.3% | Pulled               | Pulled   |  |
| M           | Salicylaldehyde + 1,3-Phenylenediamine - Schliff Base                | 5.0%                  | 7.0%  | 17.3%  | 16.5%   | 2.0%  | 10.2%                | -0.8%    |  |
| N           | Acetylacetone + 1,3-Phenylenediamine - Schliff Base                  | 44.6%                 | 43.3% | Pulled | Pulled  | -1.3% | Pulled               | Pulled   |  |
| O           | Acetylacetone + 1,2-Phenylenediamine - Schliff Base                  | 76.3%                 | 75.7% | Pulled | Pulled  | -0.6% | Pulled               | Pulled   |  |
| P           | Phthalocyanine (Kodak)   | 0.4%                  | 0.2%  | 0.0%   | -0.3%   | -0.2% | -0.2%                | 0.0%     |  |
| Q           | Cu-Phthalocyanine (Cu)   | 1.5%                  | 1.5%  | 1.4%   | 1.0%    | 0.0%  | -0.1%                | -0.4%    |  |
| R           | Meso Tetraphenyl Porphyrin   | 0.4%                  | 0.3%  | -1.4%  | -3.7%   | 0.0%  | 0.0%                 | 0.0%     |  |
| S           | Dow Corning 200  |                       | 0.2%  | -0.1%  | -0.1%   | 0.2%  | 0.0%                 | 0.0%     |  |
| T           | Phthalocyanine with Perfluoro oil                                    |                       | 0.7%  | 0.9%   | 1.3%    | 0.7%  | 0.2%                 | 0.4%     |  |
| U           | DuPont Kryptox GPL 107   |                       | 0.7%  | 0.9%   | 1.3%    | 0.7%  | 0.2%                 | 0.4%     |  |
| W           | Salicylaldehyde + Ethylenediamine in Polysiloxane                    |                       | 3.9%  | 7.9%   | 8.3%    | 3.9%  | 4.0%                 | 0.3%     |  |
| X           | Cu Chelate of Salicylaldehyde + Ethylenediamine in Polysiloxane      |                       | 0.1%  | 0.1%   | 1.6%    | 0.1%  | 0.0%                 | 1.5%     |  |
| Y           | Phthalocyanine with Polysiloxane oil                                 |                       | 0.2%  | 0.2%   | 0.4%    | 0.2%  | 0.1%                 | 0.2%     |  |
| Z           | Cu Phthalocyanine with Polysiloxane oil                              |                       | 0.3%  | 0.5%   | 1.1%    | 0.3%  | 0.2%                 | 0.6%     |  |
| AA          | meso-Tetraphenyl Porphyrin with Polysiloxane oil                     |                       | 0.1%  | 0.1%   | 0.3%    | 0.1%  | 0.0%                 | 0.2%     |  |
| AB          | Salicylaldehyde + 1,3-Phenylene Diamine in Polysiloxane              |                       | 1.2%  | 3.1%   | 3.5%    | 1.2%  | 1.9%                 | 0.4%     |  |
| AC          | Cu Chelate of Salicylaldehyde + 1,3-Phenylenediamine in Polysiloxane |                       | 0.5%  | 0.7%   | 3.3%    | 0.5%  | 0.1%                 | 2.6%     |  |

TABLE 15. SUMMARY OF CORROSION TESTS ON 52100 STEEL EXPOSED TO AIR AT 200°C

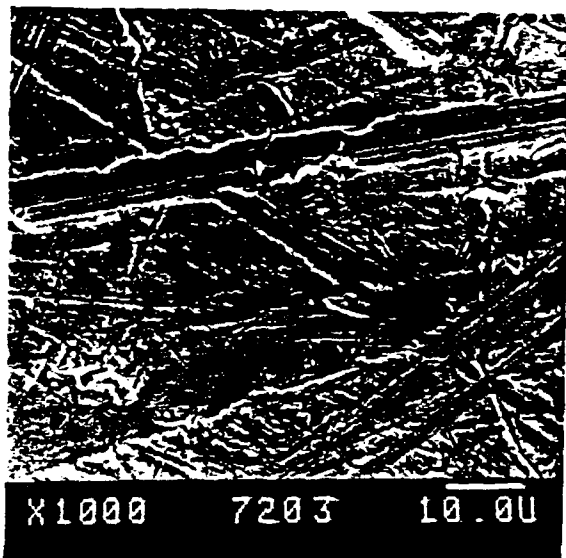
| Samples   | Weight Gain, mg/cm <sup>2</sup> |       |       |       |
|---|---------------------------------|-------|-------|-------|
|   | Exposure Time, Hours            |       |       |       |
|   | 16                              | 48    | 250   | 1000  |
| Dow Corning 200   | 0.10                            | 0.03  | 0.10  | -0.03 |
| Phthalocyanine with Perfluoro Oil   | 0.04                            | 0.6   | 0.03  | -0.01 |
| DuPont Krytox GPL 107   | -0.11                           | -0.03 | 0.06  | -0.04 |
| Salicylaldehyde + Ethylenediamine<br>in Polysiloxane Oil                        | -0.08                           | 0.00  | 2.27  | 0.15  |
| Cu Chelate of Salicylaldehyde +<br>Ethylenediamine in Polysiloxane Oil          | 0.11                            | 0.03  | 0.04  | 0.04  |
| Phthalocyanine in Polysiloxane Oil  | 0.01                            | 0.06  | 0.08  | 0.00  |
| Cu Chelate of Phthalocyanine in<br>Polysiloxane Oil                             | 0.07                            | 0.08  | 0.11  | -0.03 |
| meso-Tetraphenyl Porphyrin in<br>Polysiloxane Oil                               | 0.08                            | 0.07  | 0.11  | 0.03  |
| Salicylaldehyde + 1,3-Phenylene<br>Diamine in Polysiloxane                      | 0.06                            | 0.06  | 0.10  | 0.07  |
| Cu Chelate of Salicylaldehyde +<br>1,3-Phenylene Diamine in<br>Polysiloxane Oil | 0.11                            | 0.06  | 0.10  | 0.03  |
| MIL-G-10924E With Additives   | 0.11                            | 0.04  | -0.07 | -0.38 |
| Air (no grease)   | -0.34                           | 0.06  | 0.00  | 1.00  |
| MIL-G-10924e No Additives   | 0.03                            | 0.08  | -0.34 | -1.09 |



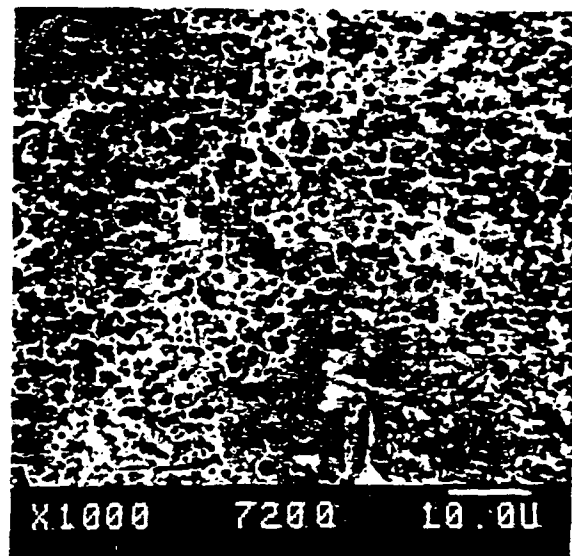
(a) No grease



(b) MIL-G-10924E  
with additives



(c) Salicylaldehyde +  
ethylenediamine in  
polysiloxane oil



(d) Meso-tetraphenyl  
porphyrin in  
polysiloxane oil

Figure 11. Photomicrographs of surface corrosion on samples of bearing steel, AISI 52100, exposed to 200°C for 1,000 hr in air and various grease formulations.



## 2.7 HIGH SPEED BEARING TEST

The high speed bearing test unit was designed for this program to evaluate high temperature greases in a dynamic environment. The grease testing machine designed and fabricated at IITRI tests the greases under a high-stress/high-speed/high-temperature condition. This would allow a more effective "real world" evaluation of the benefits of state-of-the-art lubrication additives to be made.

### 2.7.1 Equipment Design

The design of the high speed bearing test unit is given in Figure 12, which shows the assembly drawing (C06687-D-1) of the system. The unit was designed to bolt onto a standard rolling contact fatigue machine. There are eight fatigue machines at IITRI currently in working order; each one is fitted with the necessary motor-oil-control system to allow unattended operation. One of the fatigue machines was fitted with a new set of drive pulleys to take it from its current speed of 3000 rpm to the speed of the bearing unit which is 10,000 rpm. The test fixture is held in two sets of linear bearings. The thrust and radial loading for the bearing is supplied by dead weight loading through a pulley and lever arm system.

The bearing holding unit (C06687-B-2) is shown in Figure 13. This has been designed to give optimum flexibility to the unit. By replacing this holder, different types of bearings can be tested without the need for major retooling. This holder is set for a type 202K bearing and is also fitted with a thermocouple port for the control of test temperature. Temperature for the system will be supplied by a single band heater around the bearing holder. Such an arrangement allows the development of a system that is cleaner, safe, and easy to work on. Figure 14 is a photograph of the overall system, and Figures 15 and 16 are closeup views of the main unit. Power to the unit is supplied by a 3 hp-3600 rpm motor. The speed of the main shaft is 10,000 rpm, by the use of a flat mult-vee drive belt and a 2.8 pulley ratio. The power for the motor is controlled by two systems. The first is a vibration switch and the other is an amp meter. Either of these controlling devices will shut down the HSBT if vibration or torque exceeds a set value. A coupling connects the drive shaft to the center of the test bearing, and is held to the shaft by a shear pin. The shear pin is recessed behind threaded holes to prevent the

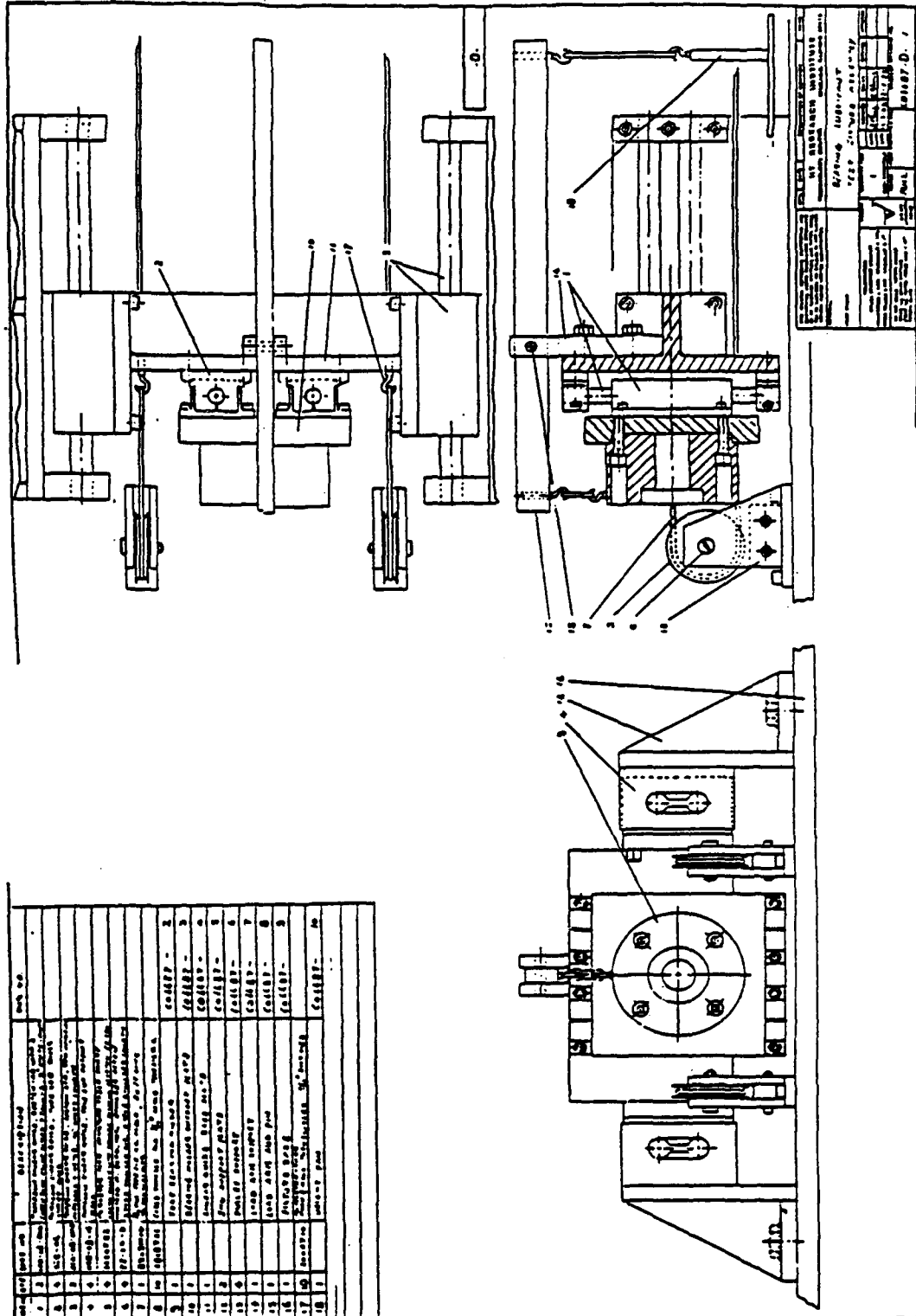
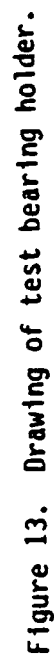


Figure 12. Assembly drawing of bearing lubricant test fixture.



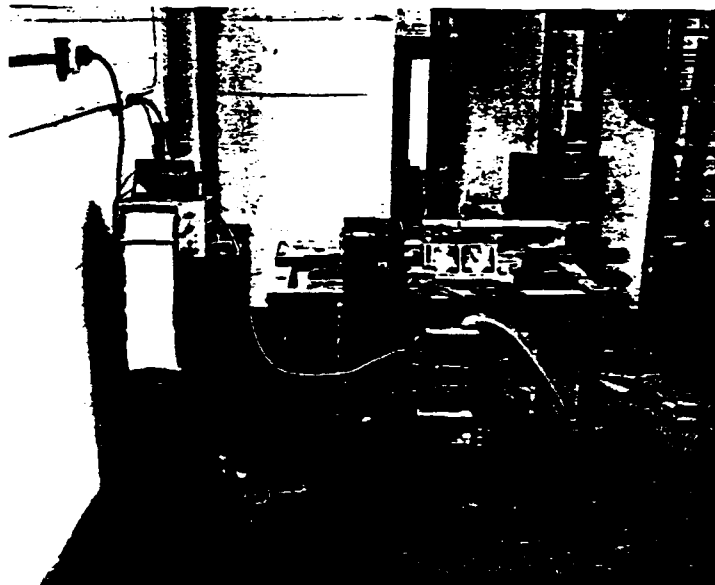


Figure 14. Overall view of high speed bearing tester.

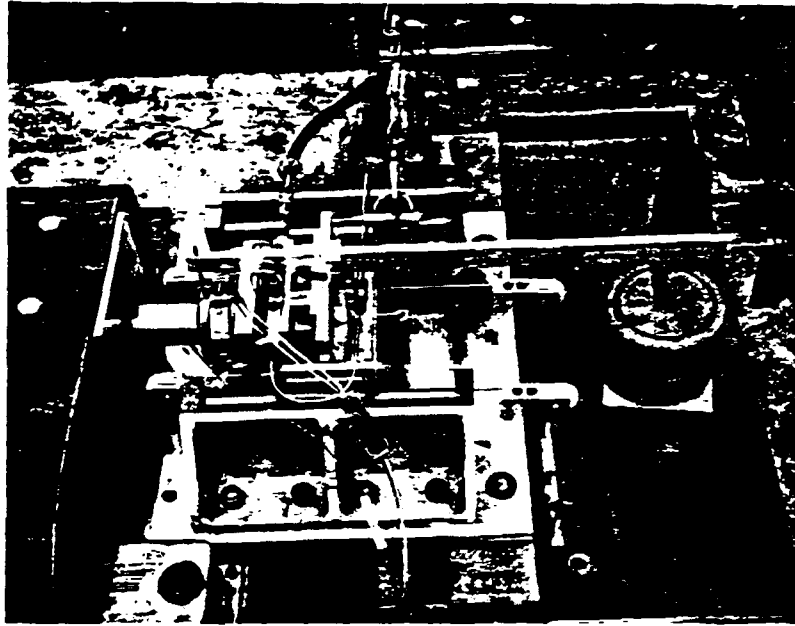


Figure 15. Side view of high speed bearing tester showing bearing assembly.

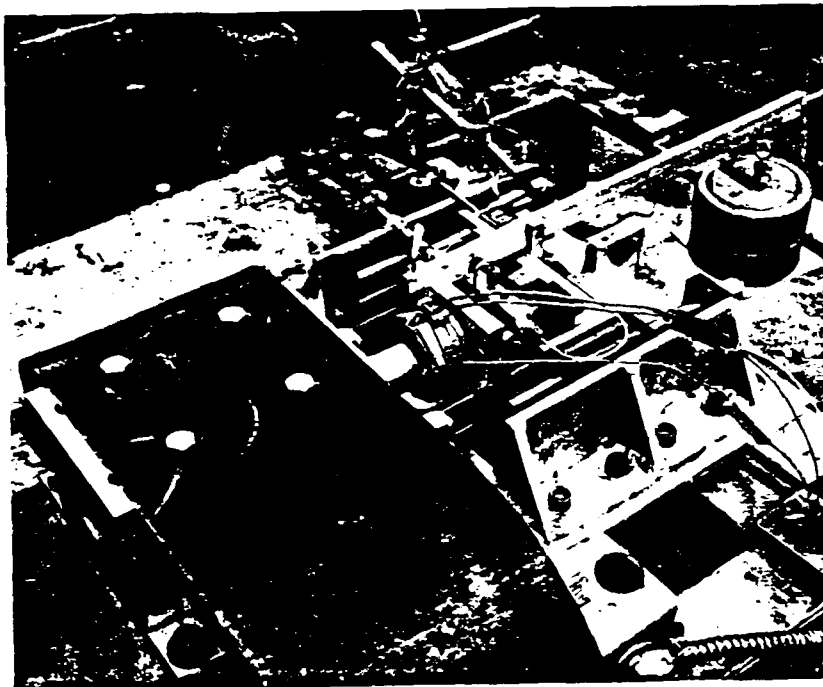


Figure 16. Side view of bearing tester showing dead weight loading system.

pin from flying out if it shears. The bearing is held inside of a block of stainless steel and is designed to require a slight press fit. The outside of the block of stainless steel has a heat tape attached which allow testing at temperatures from 50 to greater than 250°C and is regulated by a furnace controller. The block is bolted to a retainer plate which, in turn, is attached to a two degrees of freedom Thompson slide system. These slides are positioned to align freedom directions parallel to the loading directions of the bearings. In the initial system calibration, it was determined that the slide nearest the heated bearing block needed water cooling to assure proper operation. This unit was added to the system and it performed as expected. The absolute location of the cross head is monitored by a displacement transducer. The output of the transducer is fed into a strip chart recorder; and it was planned that this be used as a monitor of bearing wear. Because of the high speed nature of this bearing tester, the small amounts of wear needed to fail a bearing and the geometric design of a roller bearing it was found that this unit was not useable. Details will be given in the next section. Load is applied to the bearing by the use of dead weights. The top arm shown in Figures 15 and 16 applies the radial load and the thrust load is applied through a pulley system, also shown in these figures. The procedure for carrying out the high speed bearing test is as follows.

#### 2.7.2 Test Procedures

1. Load new bearing with 5 ml of test grease.
2. Install bearing into block and coupling assembly.
3. Install assembly in HSBT.
4. Complete system assembly, zero extensometers, turn on chart recorder and rezero clock.
5. Turn motor on and begin heating block.
6. Allow system to operate in this mode for 30 minutes.  
(This allows unit to come to equilibrium).
7. Load bearing with 50 lb thrust load.
8. Load bearing with 25 lb radial load.
9. Set ammeter to a value of 5 amps above steady state current after sample loaded.

10. Test is complete when unit shuts down because of current draw, or by the vibration switch.
11. At completion of test record, test time and remove bearing from machine.
12. Examine bearing for overall sizes of wear and record any observation.
13. Section bearing and remove four of the eight balls for micrometric analysis, and save remain balls for future analysis.
14. Clean the four balls for micrometric analysis with acetone following by soap and water to remove any remaining surface deposits.
15. Measure and record ball diameters and observation on surface quality.

## 2.8 RESULTS

A total of 29 tests have been completed in the High Speed Bearing Tester (HSBT). The data generated from these tests are presented in Table 16. A summary of the results indicating a rank order of the grease formulations evaluated in the High Speed Bearing Tests is presented in Table 17. It should be pointed out that the viscosity of each of the IITRI-lubricant formulations was substantially lower than that of the standard commercial grease used in our tests. Their viscosities should be increased and brought to par with the commercial greases in future studies. In spite of their relatively lower viscosity, two out of the five IITRI-formulations were found to be equal or significantly better than the commercial standard grease (see Table 17). Based on these initial results, we expected that if IITRI formulations were prepared at (higher) viscosities comparable to the standard commercial ones, the former would surpass the latter substantially in their wear test performance. To test this hypothesis a test was run where, in place of the polysiloxane oil, the MIL-G-10924E grease without additives was mixed with the candidate compound. When this formulation was tested it showed a failure time of 46 hours. This is more than twice the failure time exhibited by the low viscosity formulation.

Contract No. N62269-88-R-0234  
Report No. NADC-91049-60

TABLE 16. SUMMARY OF DATA FROM HIGH SPEED (10,000 RPM)  
HIGH TEMPERATURE (200°C) BEARING TESTER (1)

| Bearing No. | Grease Tested                         | Test Time, h |
|-------------|---------------------------------------|--------------|
| 0 (2)       | As received bearing                   | NA           |
| 1 (2)       | Dry (No Load)                         | 1.3          |
| 2 (2)       | MIL-G-10924E with additives           | 7.7          |
| 3 (2)       | MIL-G-10924E with additives           | 4.1          |
| 4 (2)       | MIL-G-10924E with additives (No Load) | 2.6          |
| 5           | MIL-G-10924E with additives           | 7 (3)        |
| 6           | MIL-G-10924E with additives           | 7 (3)        |
| 7           | MIL-G-10924E without additives        | 7 (3)        |
| 8           | MIL-G-10924E without additives        | 27 (3)       |
| 10          | MIL-G-10924E with additives           | 22           |
| 11          | Dry                                   | 2            |
| 12          | Type - W                              | 32           |
| 13          | As received bearing                   | NA           |
| 14          | Type - X                              | 6            |
| 15          | Type - Y                              | 4.3          |
| 16          | Type - AA                             | 8.6          |
| 17          | Type - W                              | 14.95        |
| 18          | Type - X                              | 6.3          |
| 19          | Type - Y                              | 17.7         |
| 20          | Type - AA                             | 36.8         |
| 21          | Type - W                              | 17.6         |
| 22          | Type - X                              | 8.9          |
| 23          | Type - Y                              | 14.2         |
| 24          | Type - AA                             | 34.8         |
| 30          | MIL-G-10924E with additives           | 48           |
| 31          | Type - Z                              |              |
| 32          | MIL-G-10924E with additives           | 32.4         |
| 33          | Type - Z                              | 35.5         |
| 35          | Type - Z                              | 31.2         |
| 36          | type - W modified                     | 95           |

(1) Standard test conditions are 50 lb thrust and 25 lb radial loads  
with 5 ml of grease

(2) Fafnir bearing used in these tests all other work with SKF unit

(3) Test stopped before complete failure

Type - W = Salicylaldehyde + Ethylenediamine in Polysiloxane oil

Type - X = Copper Chelate of Salicylaldehyde + Ethylenediamine in  
Polysiloxane oil

Type - Y = Phthalocyanine in Polysiloxane oil

Type - Z = Copper chelate of Phthalocyanine in Polysiloxane oil

Type - AA = Meso - Tetraphenyl Porphyrin in Polysiloxane oil

Type - W modified = 5% Salicylaldehyde - Ethylenediamine compound mixed  
with MIL-G-10924E without additives.



TABLE 17. SUMMARY OF HIGH SPEED BEARING TESTS<sup>a</sup>

| Grease Compound   | Failure Time,<br>(hr) <sup>b</sup> | Projected Failure<br>Time, h. |
|---|------------------------------------|-------------------------------|
| 5% Salicylaldehyde + Ethylenediamine<br>in MIL-G-10924E Without Additives | 46                                 | 46                            |
| meso-Tetraphenyl Porphyrin in<br>Polysiloxane Oil                         | 35.8                               | 72                            |
| Cu-Chelate of Phthalocyanine in<br>Polysiloxane Oil                       | 33                                 | 66                            |
| Salicylaldehyde + Ethylenediamine in<br>Polysiloxane Oil                  | 22                                 | 44                            |
| MIL-G-10924E With additives   | 34                                 | 34                            |
| Dry Bearing (no grease)   | 2                                  | --                            |
| Phthalocyanine in Polysiloxane Oil  | 12                                 | 24                            |
| Cu Chelate of Salicylaldehyde +<br>Ethylenediamine in Polysiloxane Oil    | 7                                  | 14                            |

<sup>a</sup>Test parameter are 50 lbs thrust load, 25 lb radial load, 5 ml of grease, tested at 10,000 RPM, and 200°C

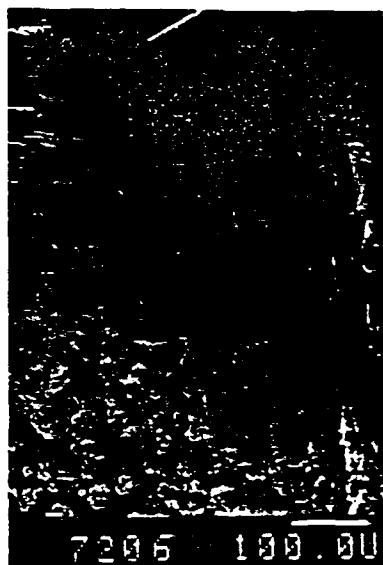
<sup>b</sup>Failure mode for test shut down is when system power draw increases by 5 amps from starting value

## 2.9 FAILURE ANALYSIS

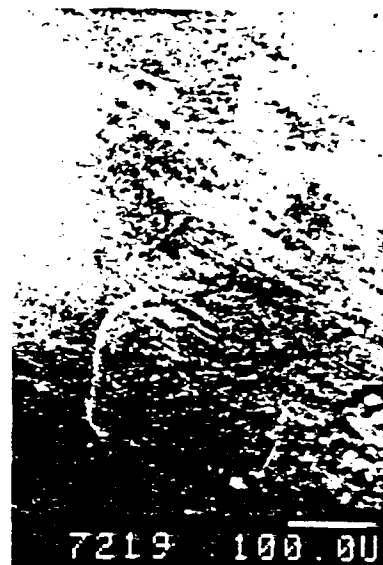
Failure analysis was done on the 39 bearings run in the HSBT. The bearing used in the HSBT is a series 200 unit with eight balls of approximately  $\frac{1}{4}$ " diameter. Analysis was concentrated on the tests where the bearings were run to failure. For each bearing, four of the eight balls were removed from the unit and cleaned. The cleaning was done with soap and water in an ultrasonic cleaner. The balls were then examined with an optical microscope at 20-30X. Representative areas along with special locations were identified by this method for further analysis. These areas were then examined in the SEM. Figure 17 a to i are SEM photographs showing the surfaces of the balls from



(a) As received



(b) Dry bearing



(c) MIL-G-10924E  
with additives



(d) Salicylaldehyde plus  
ethylenediamine



(e) Copper chelate of  
salicylaldehyde and  
ethylenediamine



(f) Phthalocyanine

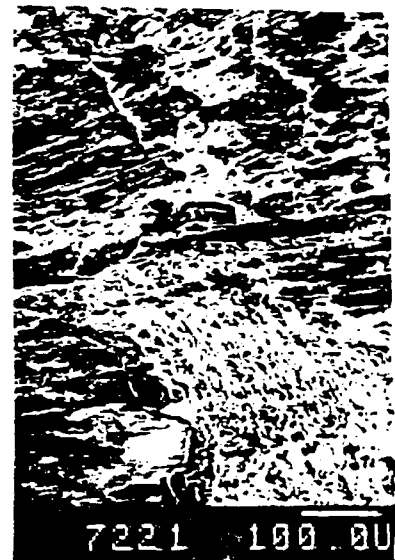
Figure 17. Surface appearance of balls taken from bearings tested at 200°C in the High Speed Bearing Tester (HSBT).



(g) Copper chelate of  
phthalocyanine



(h) Meso-tetraphenyl  
porphyrine



(i) Salicylaldehyde  
plus ethylene-  
diamine in  
MIL-G-10924  
without additives

Figure 17. Surface appearance of balls taken from bearings tested at 200°C in the High Speed Bearing Tester (HSBT) (Continued).

**Contract No. N62269-88-R-0234**  
**Report No. NADC-91049-60**

failed bearings. As these photographs show the surface appearance is highly varied. Examination of these photographs combined with the time to failure data lead to the observation that the bearings are failing in a series of steps, these are as follows:

- As the bearing is running a smooth uniform wear surface develops, as shown in Figures 17c, f, g, and h;
- as operation continues spallation of the wear surface begins, see Figure 17b, d, e, and h;
- at some point the surface spallation reaches a stage when the bearing stops;
- the amount of surface spallation present on the balls is a measure of the lubricity of the grease. The more lubricating the formulation the more spallation it will take to stop the bearing;
- Lubrication comes from two modes; first the base oil of the process contributes to the staying power of the grease. In this the base of the MIL-G is better because it does not run out of the bearing as the polysiloxane oil does. The second is the additive its present as a film and it lowers the sliding contact forces.
- Both modes are needed. In this study the MIL-G base worked the best because it stayed in the bearing and was therefore able to supply the additive to the surfaces when needed. The additives found by IITRI were slippery and able to keep the bearing working even when large amounts of surface spallations were present.
- Combining the base oils from the MIL-G with one of IITRI additives should be the best of both systems. The surface of bearing 36 shown in Figure 17i, exhibits a very rough appearance. This bearing failed after 46 hours of operation.

One by-product of the spallation of the bearing is what happens to the rejected metal. This metal is likely to move to a new location and be forge-welded onto a ball, this is shown in Figure 18.

One of the grease formulations, the copper chelate of phthalocyanine formed a very protective layer on the balls. It was not removed in the cleaning process, this is shown in Figure 19. This could be why the bearings with this grease lasted so long.

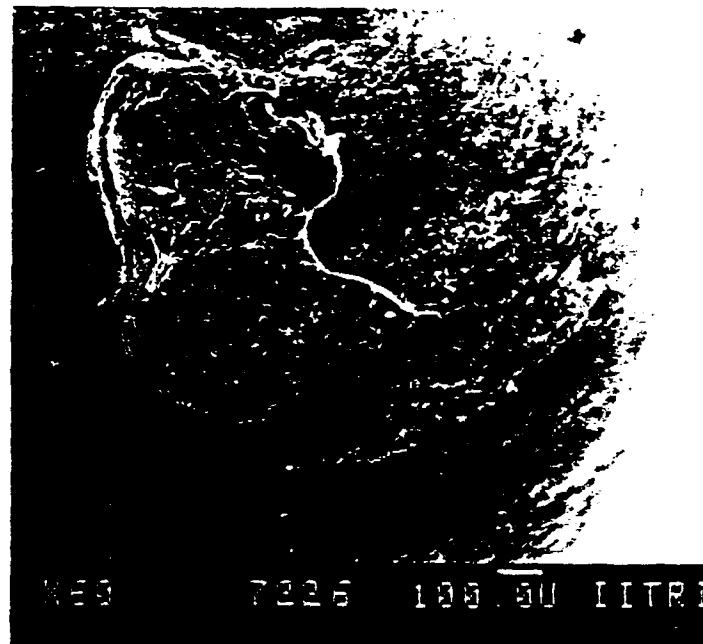


Figure 18. Welded spallation section on ball bearing.

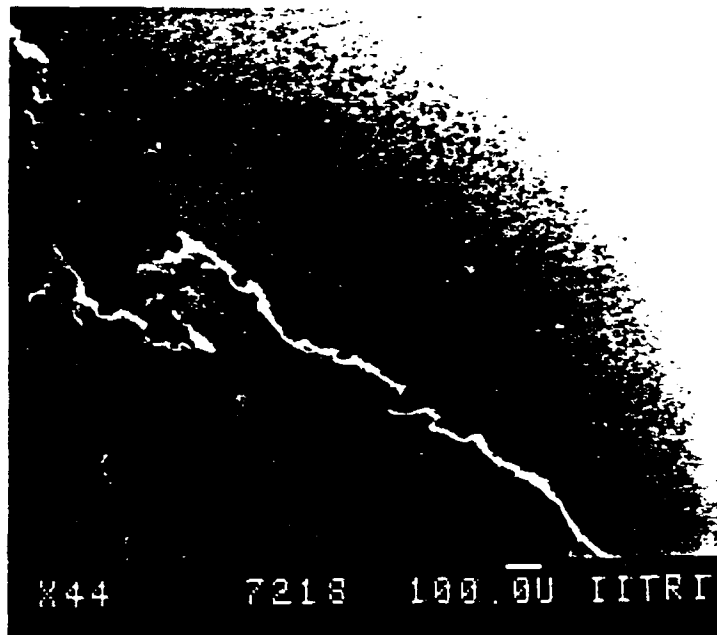


Figure 19. Surface film present on ball from bearing number 31.

## 2.10 RECOMMENDATIONS

On the basis of the results of our current research program, we strongly feel that it is necessary and very worthwhile to undertake further work as outlined below in order to realize the objective of this research effort, viz., the development of a substantially improved high temperature lubricant system involving a somewhat unique class of macrocyclic compounds and their metal chelates. Following is a brief outline of the proposed work:

1. To prepare and characterize four selected Schiff bases, two phthalocyanines, and two porphyrins suitable for use in our lubricant formulations; the candidate compounds are selected on the basis of their promising (overall) performance characteristics exhibited in the preliminary testing in our current study;
2. to investigate and optimize the grease formulations prepared by using the selected macrocyclic compounds, the study will involve the use of two different base materials, viz., (i) base oils, and (ii) MilSPEC neutral grease, the proposed additive levels are: (i) 5%, (ii) 20%, and (iii) 40%; the same final viscosity will be maintained in each case by including varying amounts of appropriate inert fillers;
3. to carry out the above for two of our candidate compounds (additives) and if successful extend to the rest of the selected compounds;
4. the studies under (2) and (3) will include: (i) preparation of the formulation; (ii) characterization of the formulations, viz., viscosity and thermal stability; (iii) corrosion protection and wear resistance tests;
5. to investigate the possible use of our candidate compounds as lubricants in their own right; this will involve their deposition by the "solution-mixing and baking" mode and "multimolecular layer coating under vacuum" mode; after characterizing the nature of the coating, tests on the corrosion- and wear-preventive characteristics will be carried;
6. to carry out the wear test studies as follows:
  - a. to test at the standard conditions with a base grease to determine data variation;
  - b. to test at the standard condition using bearings from different manufacturers to determine the effect of manufacturing variation;

- c. to test at various loads with a base grease to determine stress effect;
  - d. to test at selected temperatures with a base grease to determine the effect of temperature; and
  - e. to modify equipment to yield torque measurements to allow the determination of friction factors; and
7. to examine the data on the wear-resistance and corrosion protection characteristics in the perspective of the chemical structure, surface-binding, and stability characteristics of the candidate compounds and consider the possibility of developing a mechanism of their action in the lubricant formulation.



**APPENDIX 1**

**DIFFERENTIAL SCANNING CALORIMETRIC THERMOGRAMS  
OF SCHIFF BASE COMPOUNDS**

Figure 1. DSC-Thermogram of Compound No. 1 (Table 9A):  
Sealed Pan in Nitrogen Atmosphere

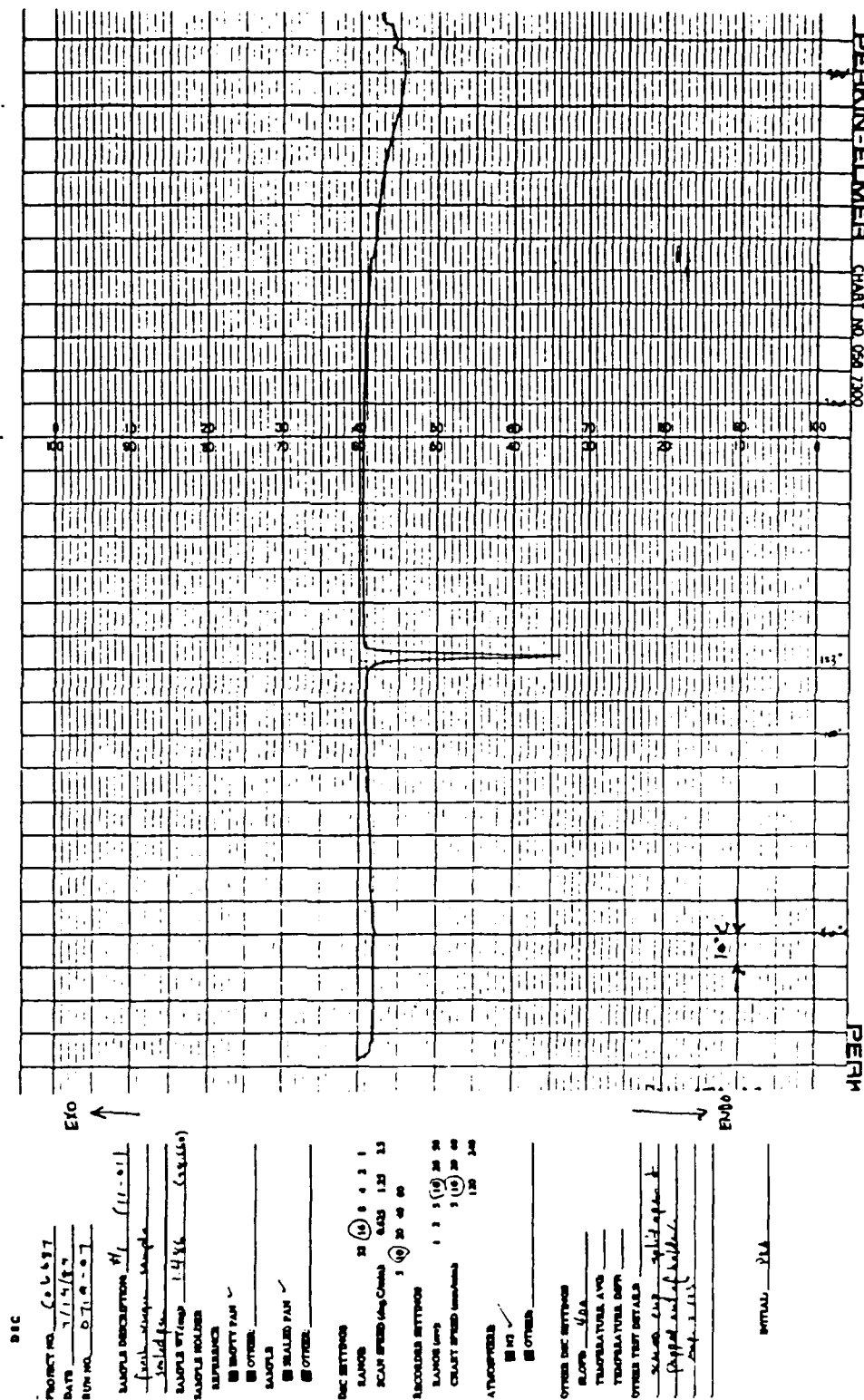
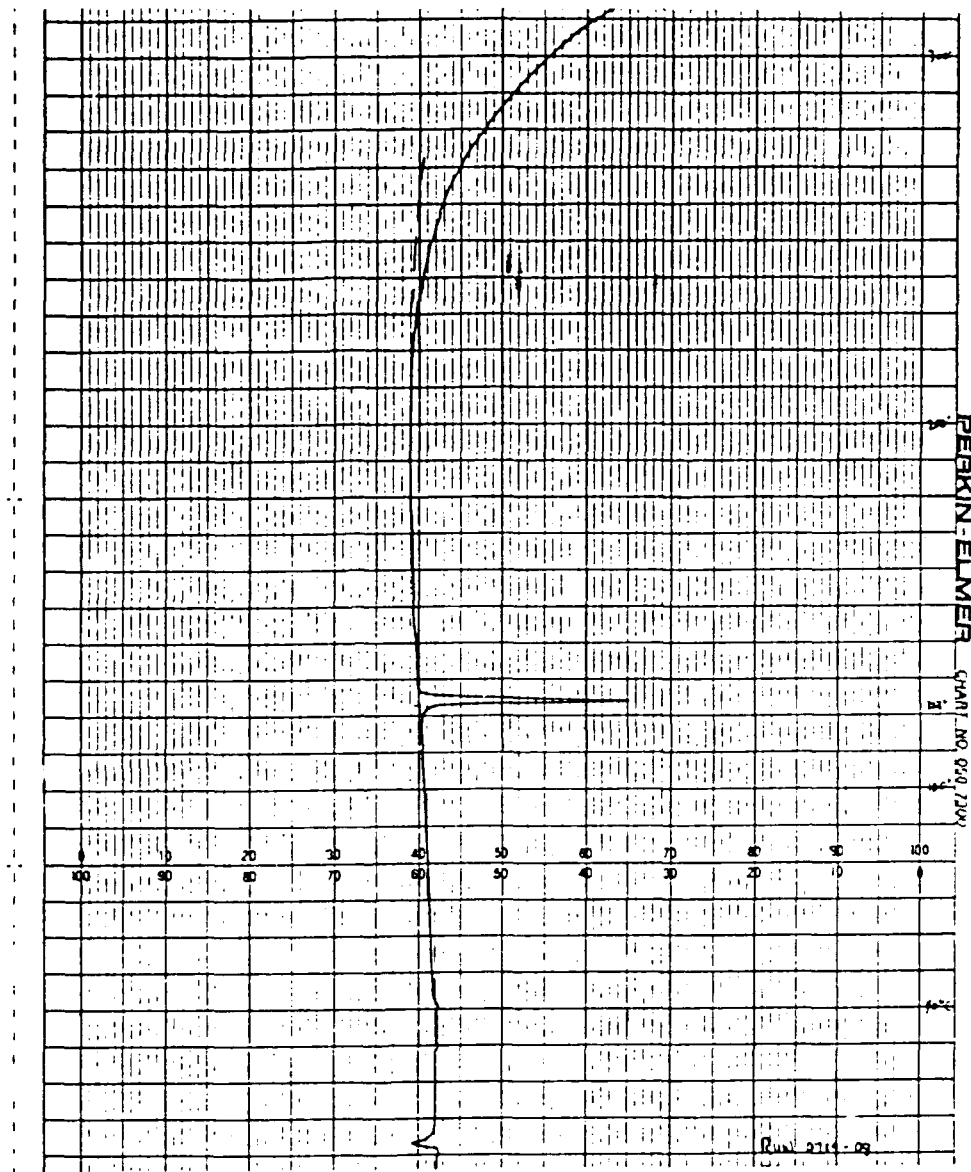


Figure 2. DSC-Thermogram of Compound No. 1 (Table 9A):<sup>a</sup>  
Vented Pan in Nitrogen Atmosphere



PROJECT NO. 06687  
 DATE 7/1/52  
 RUN NO. 0179-04  
 SAMPLE DESCRIPTION 1 (11-02)  
 NAME WATER  
 SAMPLE WT (gms) 1372 (23.64)  
 SAMPLE HOLDER  
 REPURPOSE  
☒ EMPTY PAN ✓  
☐ OTHER  
 SAMPLES  
☒ SEALED PAN  
☐ OTHER vented sealed pan  
 DEC SETTINGS  
 BLANKS 32 (16) 0 4 3 1  
 SCAN SPEED (deg/Chan) 0.25 1.25 2.5  
 5 (10) 20 40 60  
 RECORDS SETTING  
 BLANKS (sec) 1 2 5 (10) 20 30  
 CHART SPEED (mm/min) 3.00 20 30 60  
 120 240  
 ATMOSPHERES  
☒ H<sub>2</sub>  
☐ OTHER  
 OTHER DEC SETTINGS  
 SLOPE 65U  
 TEMPERATURE AND  
 TEMPERATURE CORP  
 OTHER TEST DETAILS  
 VOLATILIZATION FIELD ☐

INITIAL DA

300

PROJECT NO. C66687  
DATE - 7/10/87  
FROM NO. 0710-12

03/26/87 3:14  
11-03 4 SOLIDUS FLOW

\_\_\_\_\_

✓  
BOATHOUSE  
WATER FRONT

☐ OTHER \_\_\_\_\_  
☐ \_\_\_\_\_  
☐ \_\_\_\_\_

☒ SEALED PAID  
☐ OTHER: VENTED, SEALED MAN

**DECLASSIFIED**

| SAMPLE                   | IN | (6)   | 0    | 4   | 3 | 1 |
|--------------------------|----|-------|------|-----|---|---|
| SCALE SPEED (Avg Counts) |    | 9.428 | 1.29 | 1.5 |   |   |

100-20420

RECORDED 11/11/42

INDEXED 11/11/42

CLARK FRED (mrs. John)

**A TYPICAL**

**NO**

**A ZEP. A.R.**

OTHER DEC MATTERS

SLABS 400  
TEMPERATURE, AVO. \_\_\_\_\_

TELEPHONE NO. \_\_\_\_\_  
OTHER TTY DETAILS \_\_\_\_\_  
CWA CODE (A-1) \_\_\_\_\_

0.512" DIA

---

normal pink

---

**Figure 3.** DSC-Thermogram of Compound No. 2 (Table 9A):  
Vented Pan in Air Atmosphere

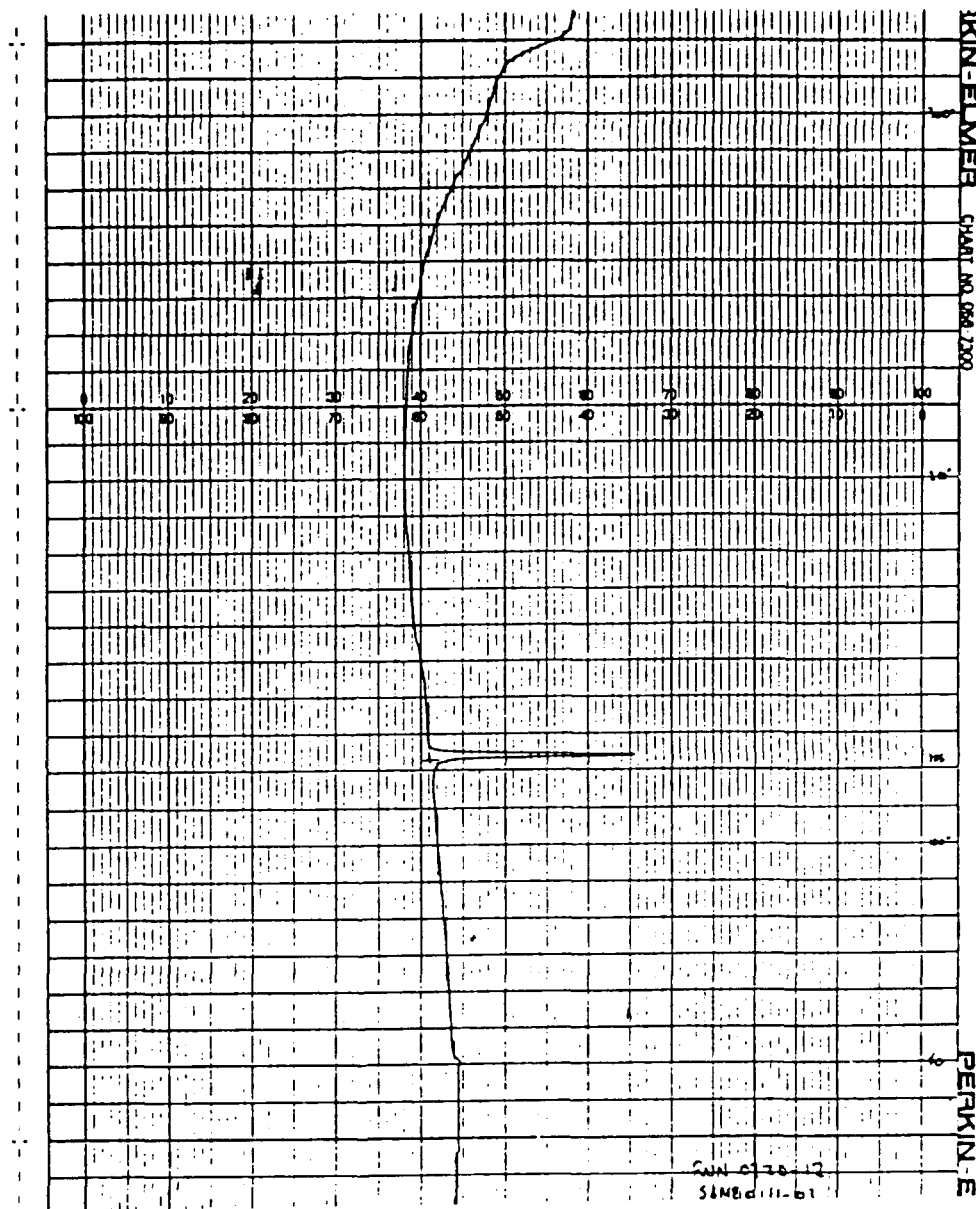


Figure 4. DSC-Thermogram of Compound No. 2 (Table 9A):  
Sealed Pan in Nitrogen Atmosphere

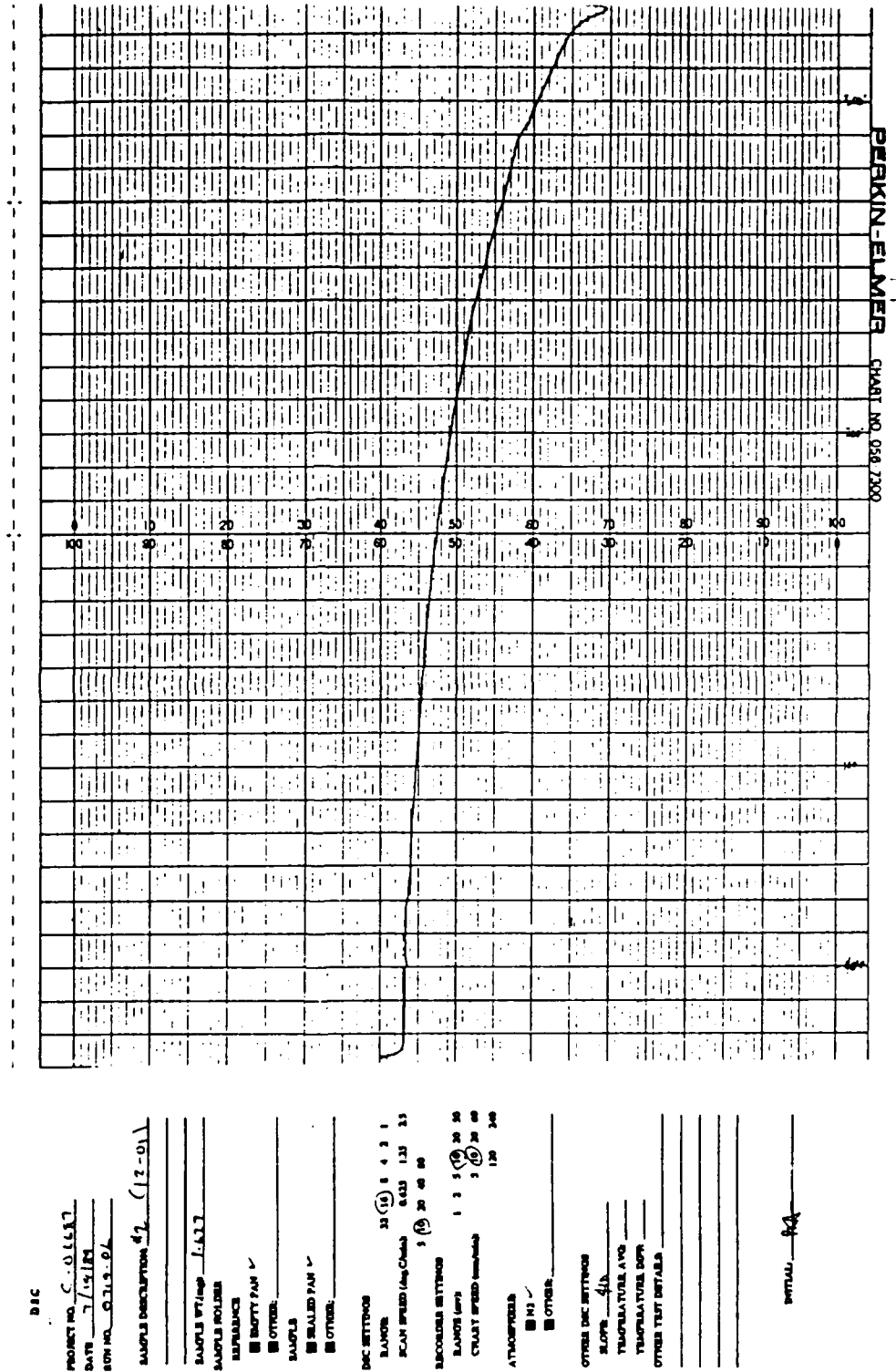
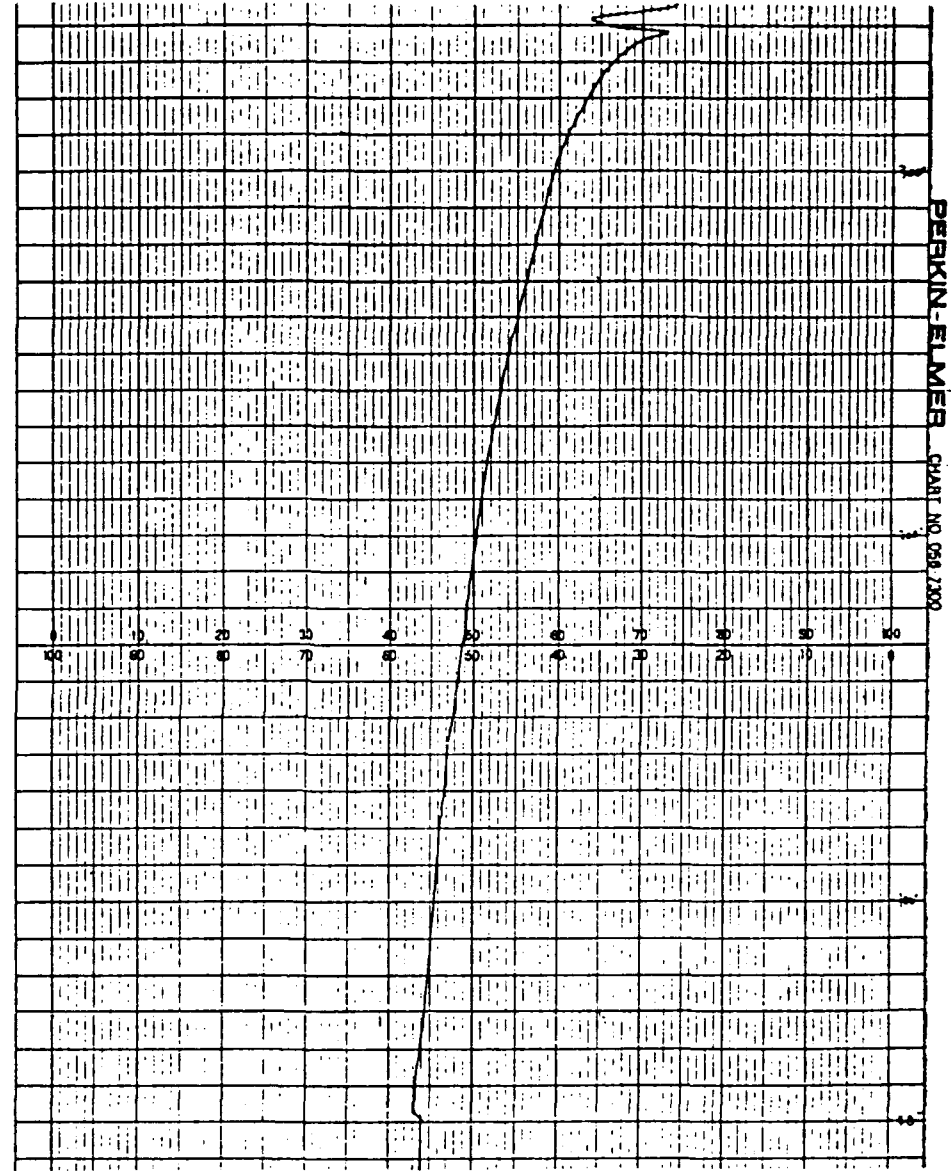


Figure 5. DSC-Thermogram of Compound No. 2 (Table 9A):  
Vented Pan in Nitrogen Atmosphere



DSC

PROJECT NO. 50117  
DATE 7/1/89  
RUN NO. 0718-01

SAMPLE DESCRIPTION #2 (17-02)  
VENTED PAN

SAMPLE WT (mg) 13.12 (31.14)  
SAMPLE HOLDER  
REFERENCE  
☐ EMPTY PAN  
☐ OTHER  
SAMPLE  
☐ SEALED PAN  
☐ OTHER VENTED D. 42 ALIP (P6)

DSC SETTINGS  
SCAN RATE 10 °C/min  
SCAN SPEED (mg/min) 0.433 1.33 3.3  
1.00 20 40 80

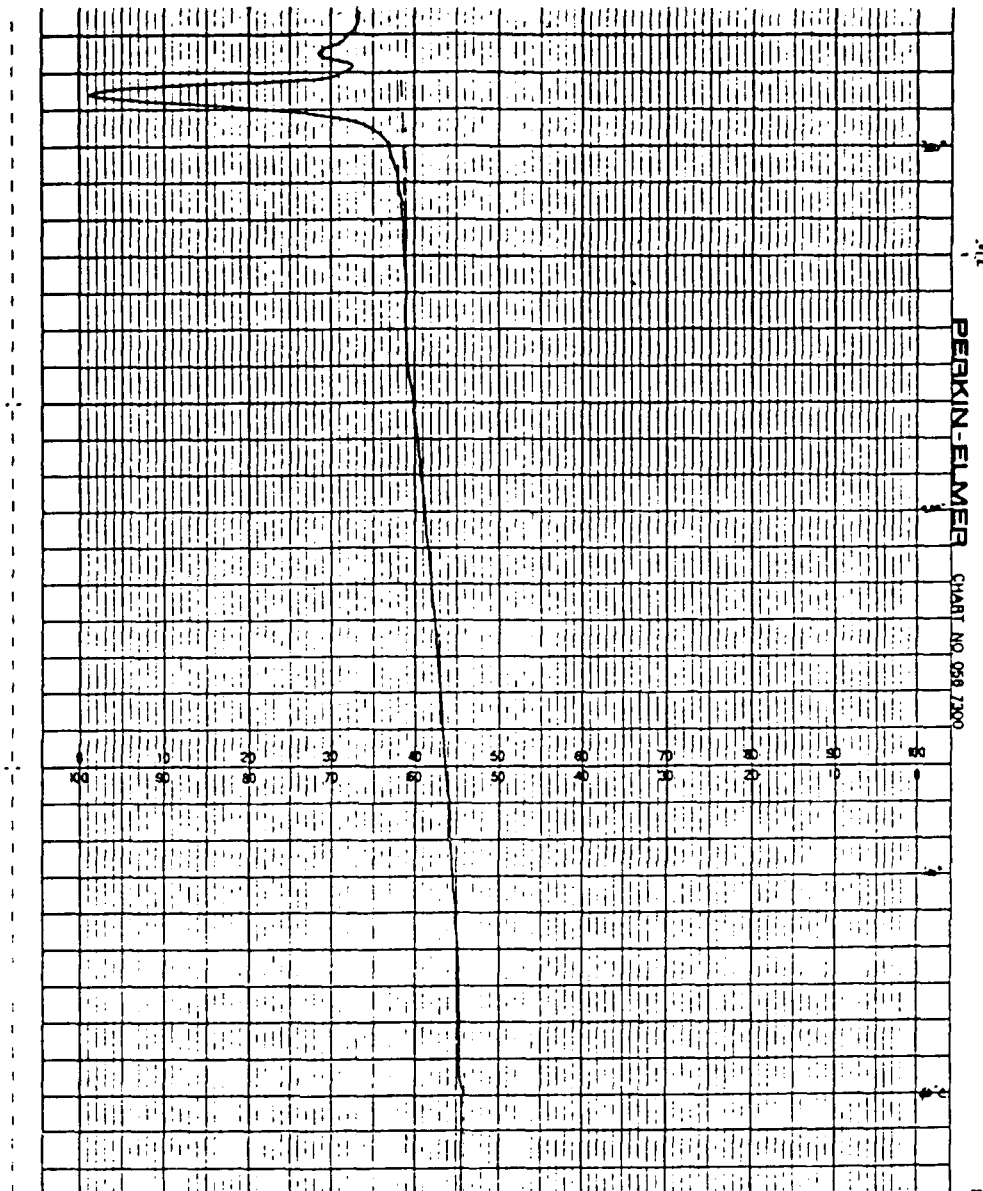
RECORDED SETTINGS  
SCAN RATE 10 °C/min  
SCAN SPEED (mg/min) 0.433 1.33 3.3  
1.00 20 40 80

ATMOSPHERE  
☒ N2  
☐ OTHER

OTHER DSC SETTINGS  
FLOW 100 mL/min  
TEMPERATURE AVO  
TEMPERATURE DOP  
OTHER TEST DETAILS

ANALYST RA

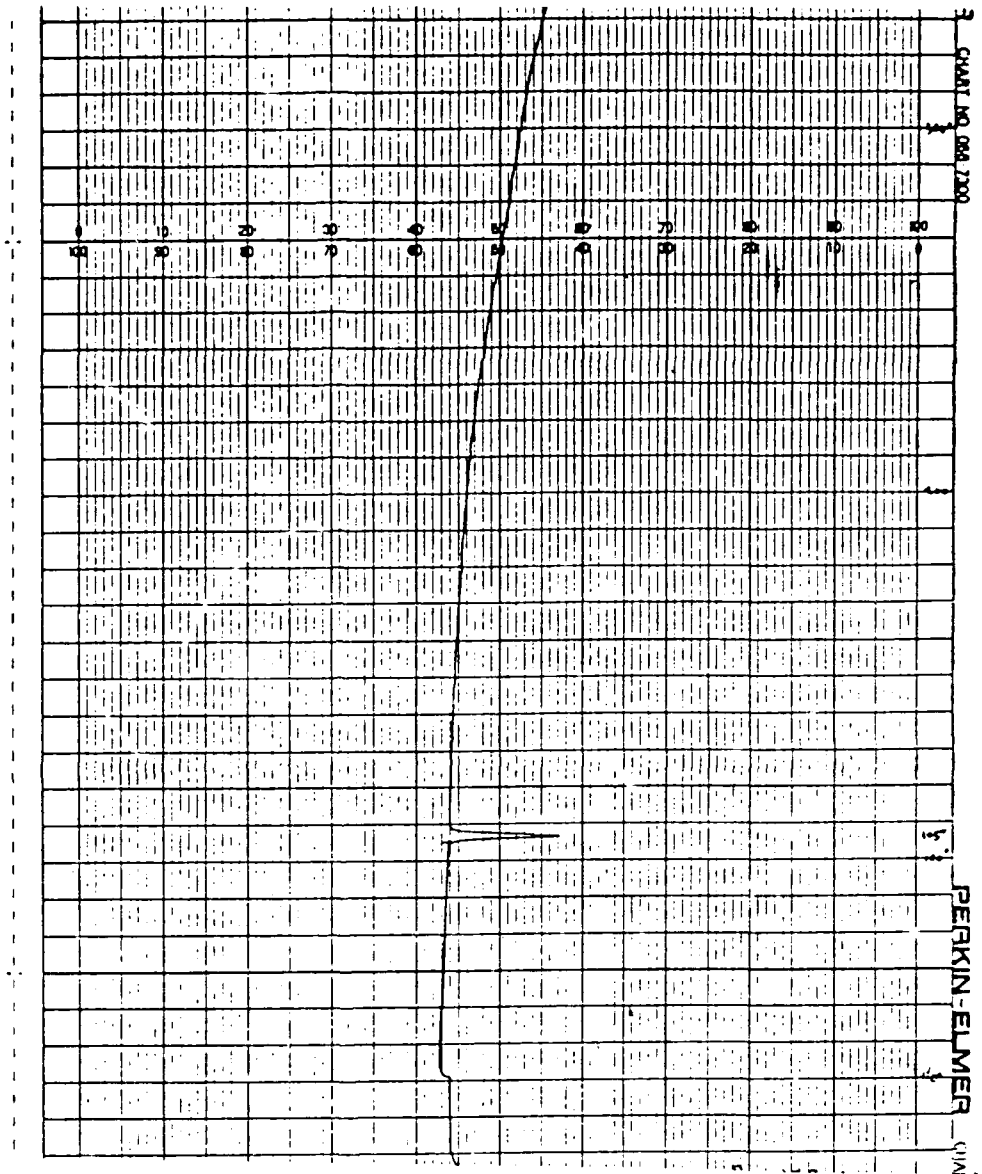
Figure 6. DSC-Thermogram of Compound No. 2 (Table 9A):  
Vented Pan in Air Atmosphere



DSC  
PROJECT NO. C06587  
DATE 7/11/89  
ROW NO. 0221-02  
SAMPLE DESCRIPTION 37 (12.05)  
AIR, AIR DRY, VENT IN COMB  
SAMPLE WT/amp 1.145 (1.145)  
SAMPLE HOLDER  
☒ BAKED PAN  
☐ OTHER  
SAMPLE  
☒ BAKED PAN  
☐ OTHER  
DSC SETTINGS  
RANGE 20 10 1 4 1 1  
SCAN SPEED (deg/min) 6.25 1.25 1.5  
RECORDED SETTINGS  
SAMPLE WT 1 2 3 4 5 6 7 8 9 10  
CHART SPEED (mm/min) 10 20 40 80  
ATMOSPHERE  
☒ N2  
☐ OTHER TRE AIR  
OTHER DSC SETTINGS  
→ SLOPE 420  
TEMPERATURE APO  
TEMPERATURE DEPT  
OTHER TEST DETAILS

DETAIL 102

Figure 7. DSC-Thermogram of Compound No. 3 (Table 9A):  
Sealed Pan in Nitrogen Atmosphere



DSC

PROJECT NO. C65587  
DATE 7/17/89  
RUN NO. 0111-0

SAMPLE DESCRIPTION 63 (13.01)  
SEALER NA

SAMPLE WT (mg) 0.810 (17.70)  
SAMPLE HOLDER  
REFERENCE  
EMPTYPAN ✓  
OTHER:  
SAMPLE  
SEALDPAN ✓  
OTHER:

DSC SETTINGS  
SCAN 25 0 0 4 3 1  
SCAN SPEED (deg/min) 0.433 1.25 2.5  
3.00 20 40 80

RECORDER SETTINGS  
SCAN (sec) 1 3 5 10 20 40  
CHART SPEED (mm/min) 5 10 20 40  
1.20 2.40

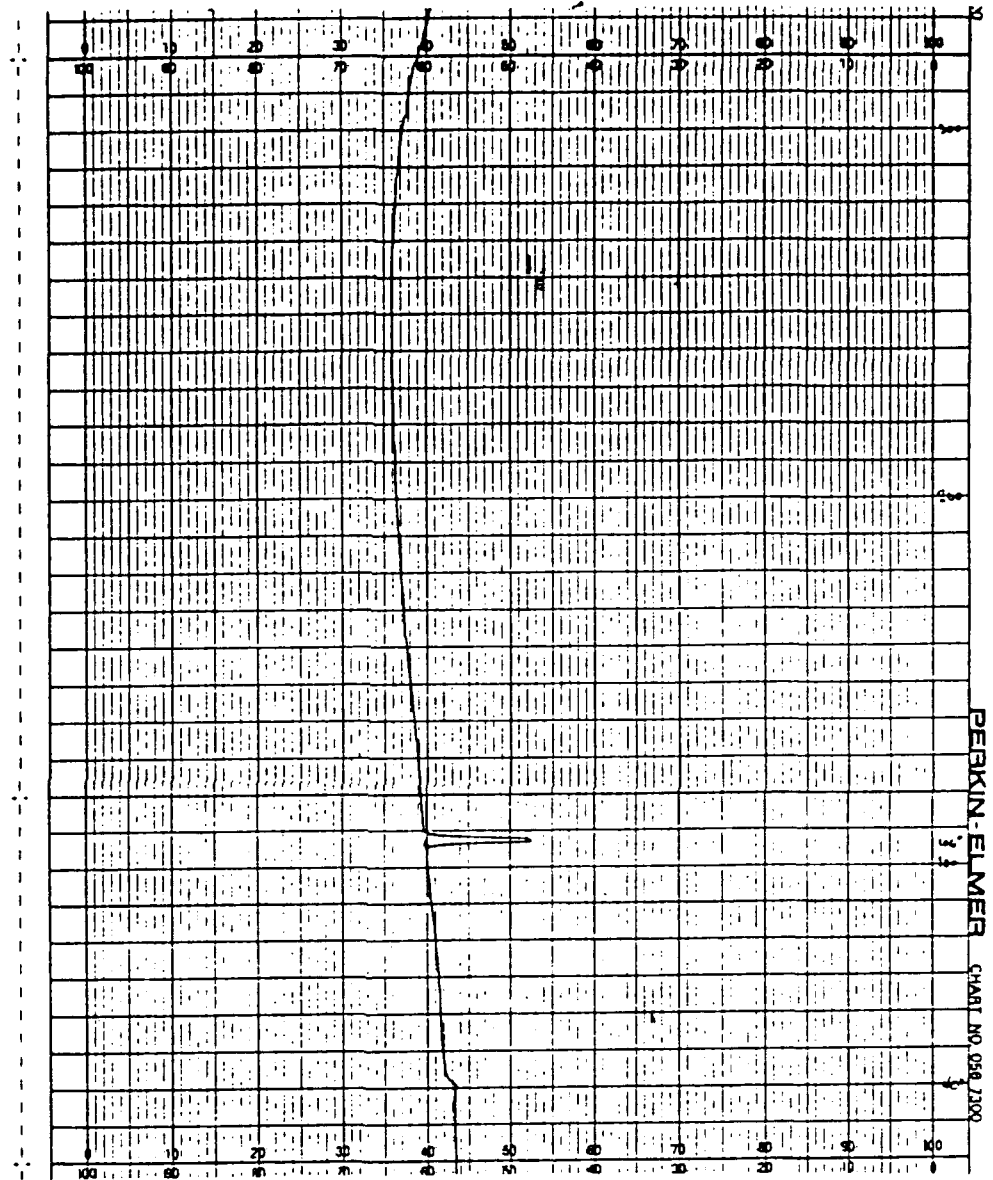
ATMOSPHERE  
N2 ✓  
OTHER:

OTHER DSC SETTINGS  
BLANK 310  
TEMPERATURE APO  
TEMPERATURE DOP  
OTHER TEST DETAILS

INITIAL *DP*



Figure 8. DSC-Thermogram of Compound No. 3 (Table 9A):  
Vented Pan in Nitrogen Atmosphere



DSC

PROJECT NO. COLLEY7  
DATE 7/18/87  
RUN NO. 0119-11

SAMPLE DESCRIPTION #3 (13-02)  
VARIANT N

SAMPLE WT/IMP 0.938 (11.3u)  
SAMPLER SOURCE  
REFERENCE  
☒ BOTTLE PAN  
☐ OTHER

SAMPLE  
☒ SEALED PAN  
☐ OTHER VENTED PAN

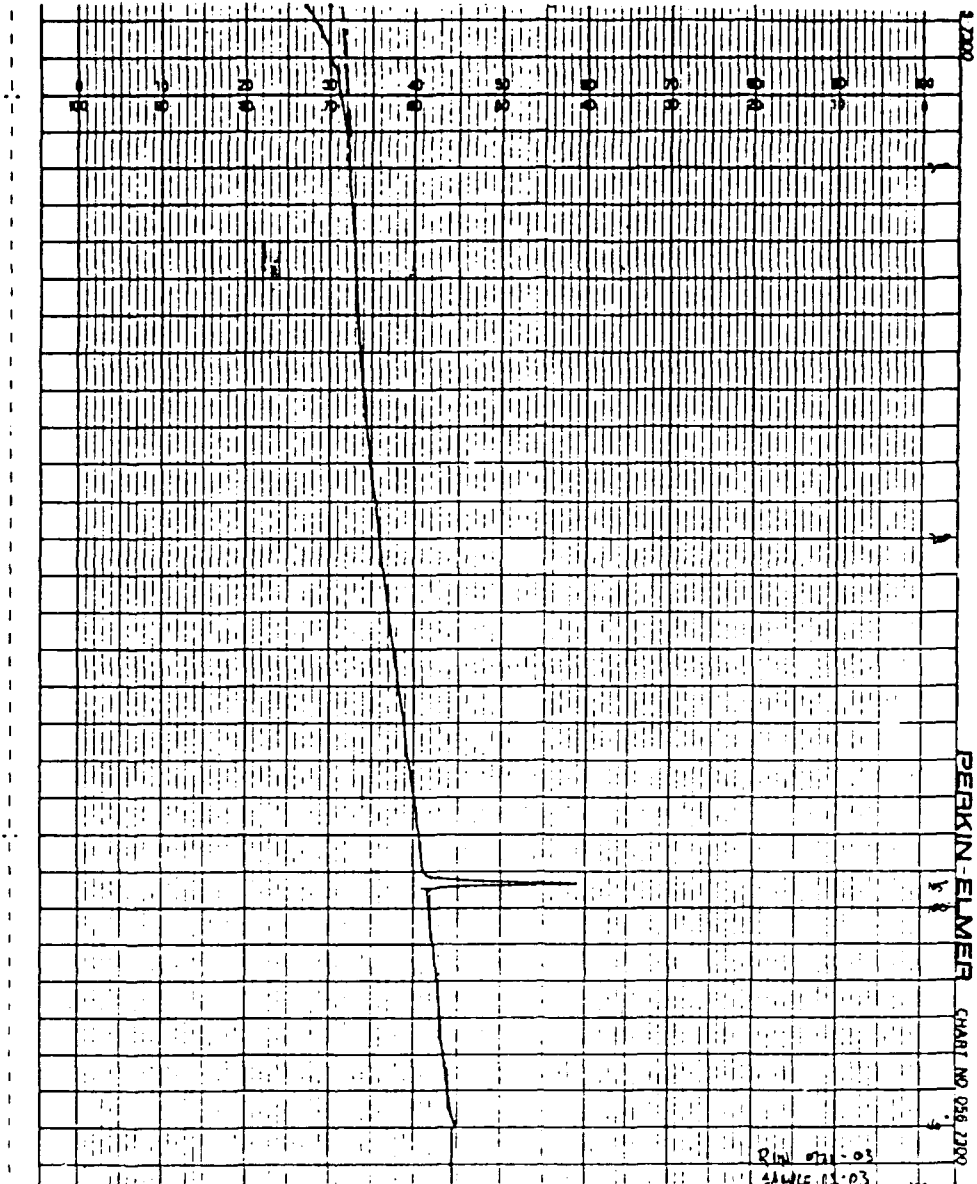
DSC SETTINGS  
SCAN RATE 10 (1) 0 1 2 1  
SCAN SPEED (deg/min) 0.03 1.15 2.5

RECORDING SETTINGS  
SCAN RATE 1 3 5 10 20 30  
CHART SPEED (mm/min) 5 10 20 40  
ATTACHMENTS ☒ HJ  
☐ OTHER

OTHER DSC SETTINGS  
SLOPE 5.5e-10  
TEMPERATURE AVO  
TEMPERATURE DOP  
OTHER TEST DETAILS

INITIAL DV

Figure 9. DSC-Thermogram of Compound No. 3 (Table 9A):  
Vented Pan in Air Atmosphere



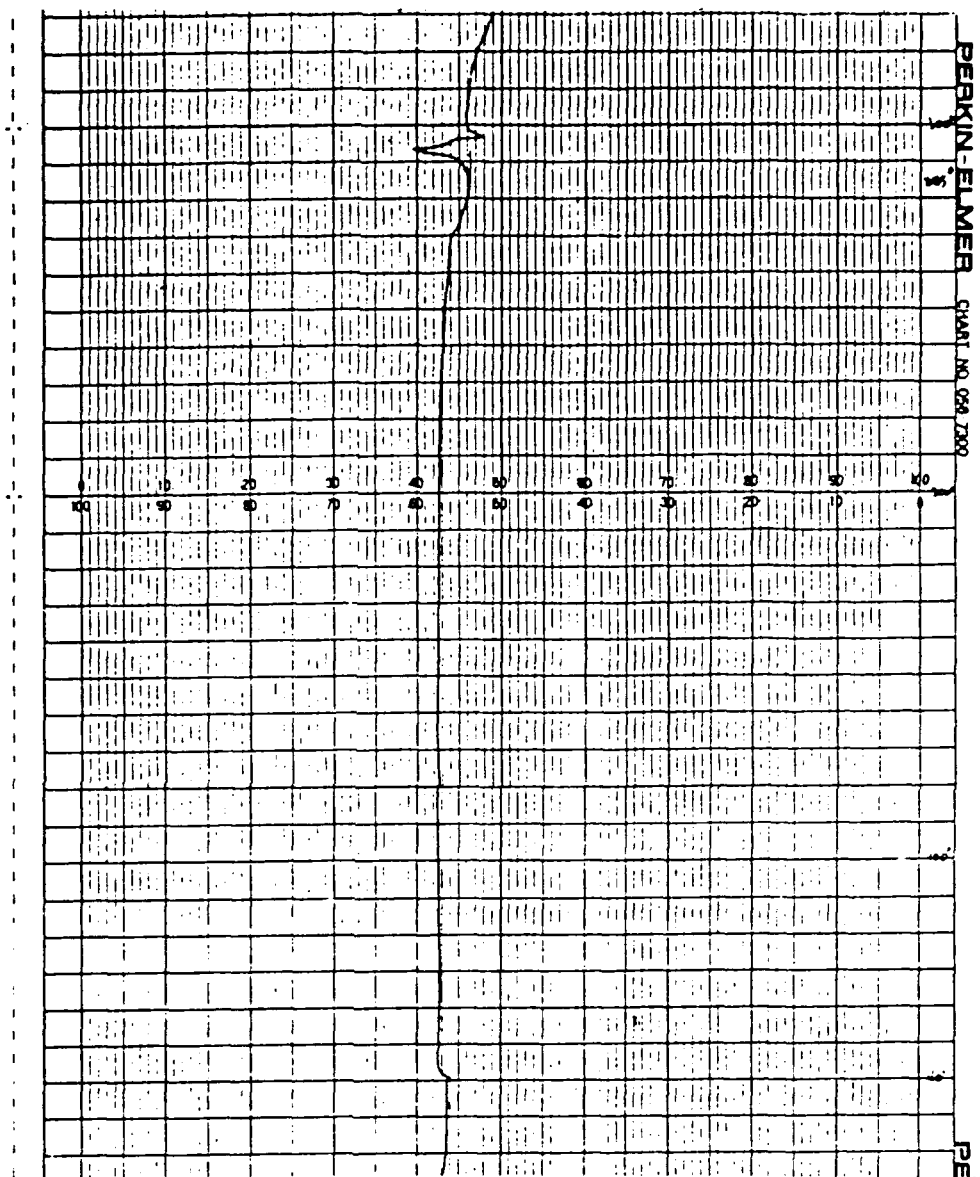
PROJECT NO. 006687  
 DATE 7/21/87  
 ROW NO. 0731-03  
 SAMPLE DESCRIPTION #3 (13-03)  
SELECTED - ZERO AIR  
 SAMPLE WEIGHT 0.901 (27.51)  
 SAMPLE BOLDS  
 SURFACES  
☒ BROTT PAN ✓  
☐ OTHER:  
 SAMPLES  
☒ RECALLED PAN  
☒ YES - VENTILATED (SEE 13-06A)

1  
 22 13 1 4 2 1  
 -SD (Avg Chnals) 0.433 1.30 2.5  
 5 19 20 40 60  
 20 SETPOINTS  
 1 3 5 10 20 50  
 100  
 SPEED (cm/min) 5 10 20 40 60  
 120 240  
 PRESS  
 IF NO  
 IN OTHER: ZERO AIR

SEE 13-06 SETPOINTS  
 SLOP 47.0  
 TEMP 17.0 AND  
 TEMP 17.0 AND  
 OTHER TEST DETAILS

INITIAL: DJA

Figure 10. DSC-Thermogram of Compound No. 4 (Table 9A):  
Sealed Pan Nitrogen Atmosphere



DSC

PROJECT NO. C-61137  
DATE 7/14/83  
RUN NO. 0112-17

SAMPLE DESCRIPTION 44 (14-01)  
SEALING 44

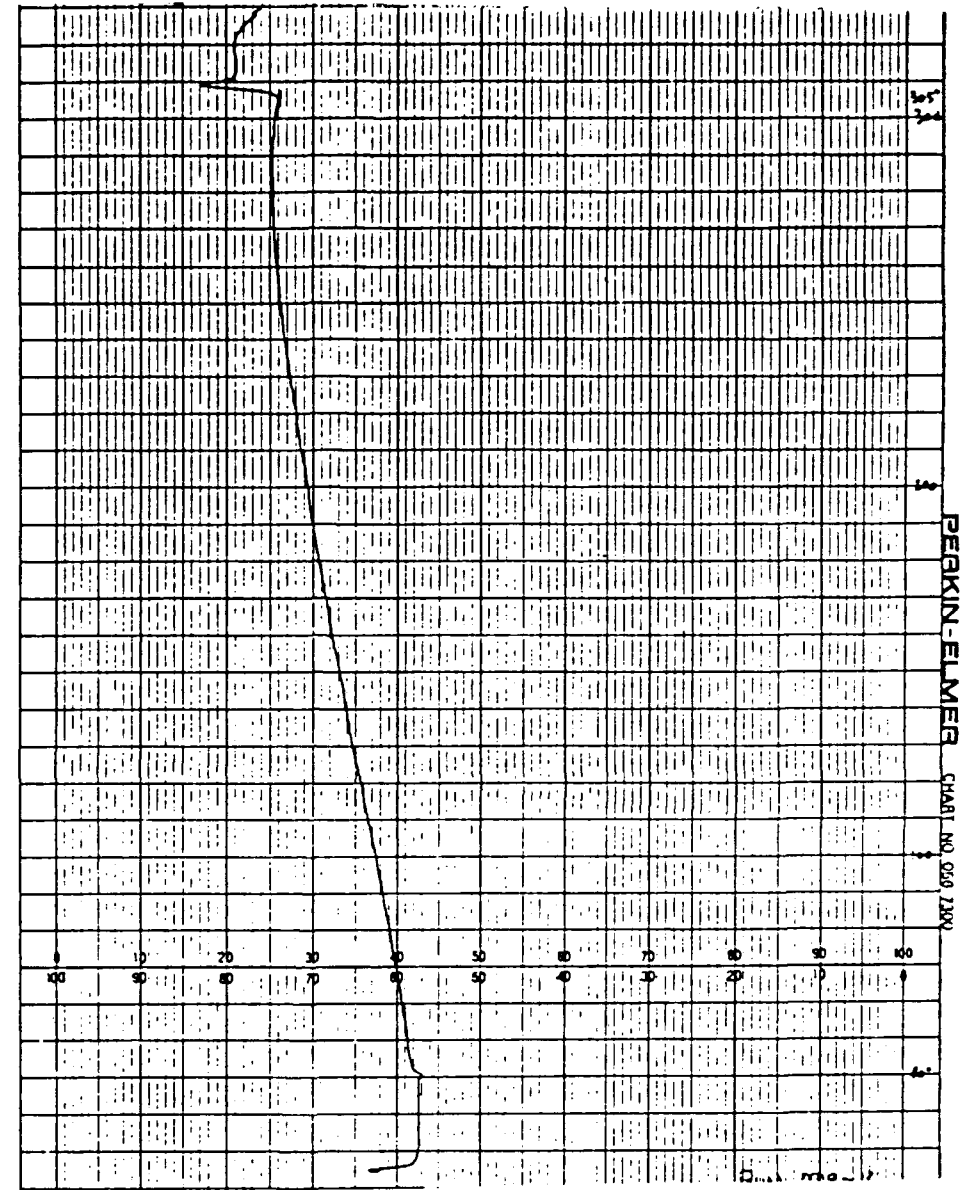
SAMPLE WT (mg) 1.333 (0.011)  
SAMPLE HOLDER  
SURFACE  
☒ BOTT PAN  
☐ OTHER  
SAMPLE  
☒ SEALED PAN  
☐ OTHER

DSC SETTINGS  
RANGE 31 (10) 0 1 2 3 4 5  
SCAN SPEED (deg/min) 5.0 1.0 1.0 1.0 1.0 1.0  
RECORDING SETTINGS  
RANGE (mV) 1 3 5 (10) 20 50  
CHART SPEED (mm/min) 3 (10) 20 50 100 200  
ATMOSPHERE  
☒ N2  
☐ OTHER

OTHER DSC SETTINGS  
SLOPE 3.73  
TEMPERATURE AVO  
TEMPERATURE BOP  
OTHER TEST DETAILS

ATTN: PUA

Figure 11. DSC-Thermogram of Compound No. 4 (Table 9A):  
Vented Pan in Nitrogen Atmosphere



DSC

PROJECT NO. C06687  
DATE 7/12/89  
RUN NO. 0719-15

SAMPLE DESCRIPTION #4 (4-02)  
VENTED N<sub>2</sub>

SAMPLE WT (mg) 1.974 (134517)  
SAMPLE HOLDER  
EQUILIBRATION  
☒ EMPTY PAN  
☐ OTHER

SAMPLE  
☒ SEALED PAN  
☐ OTHER VENTED SEALED PAN

DSC SETTINGS  
BLANKS 1 (4) 1 1 1  
SCAN SPEED (deg/min) 5 (4) 1 1 1  
1 (4) 20 40 80

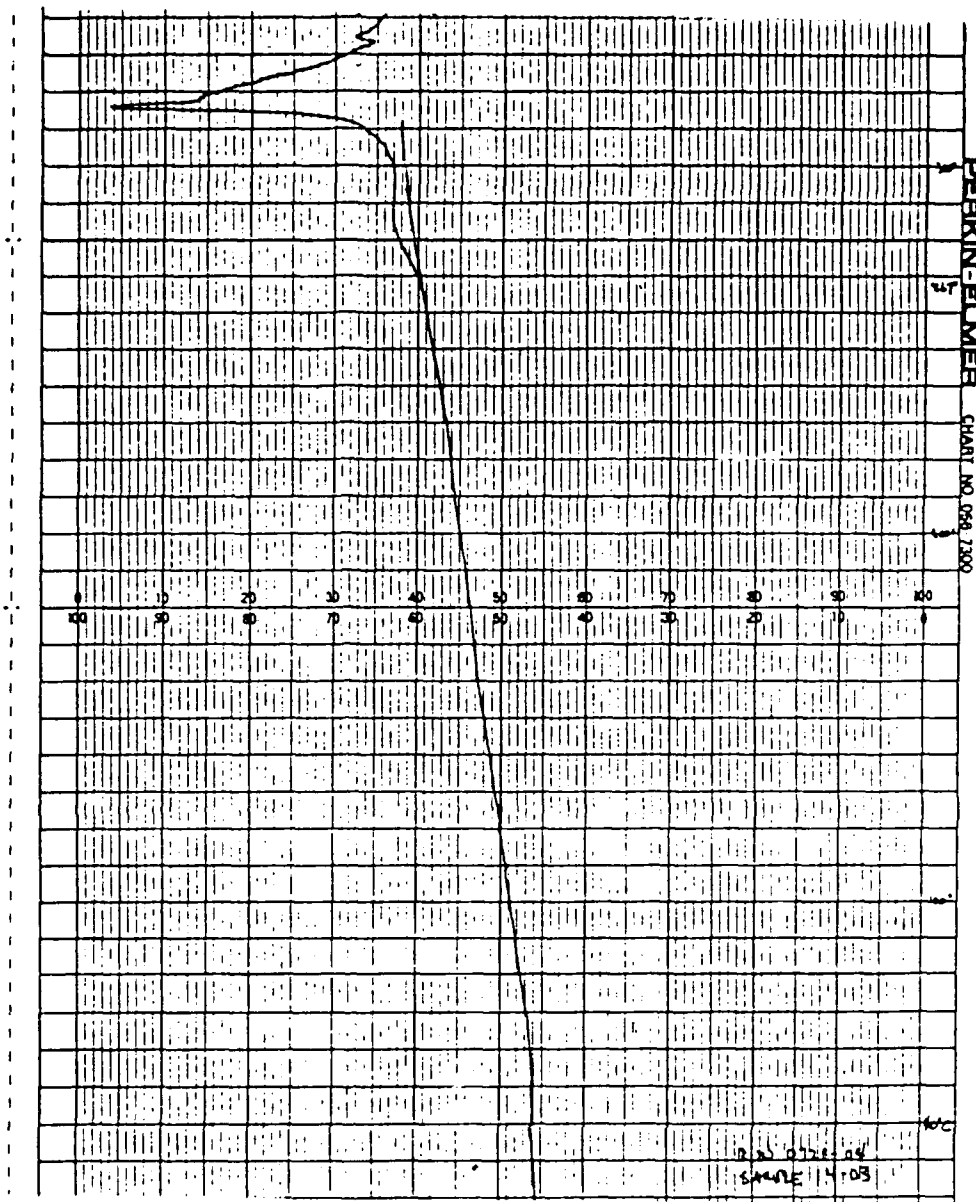
RECORDER SETTINGS  
BLANKS (mm) 1 1 1 (4) 20 40  
CHART SPEED (mm/min) 1 (4) 20 40  
120 240

ATMOSPHERE  
☒ N<sub>2</sub>  
☐ OTHER

OTHER DSC SETTINGS  
SLOPE 370  
TEMPERATURE AVG  
TEMPERATURE DIFF  
OTHER TEST DETAILS

INITIAL PJA

Figure 12. DSC-Thermogram of Compound No. 4 (Table 9A): Vented Pan in Air Atmosphere



PROJECT NO. 506687  
DATE 7/21/89  
SON NO. 0771-04

SAVING DESCRIPTION #4 (14-03)  
VIENTED, IN ZELE AIR

127.2 807/24 175077

☐ EMPTY PAN ✓

**NAME**  
**REALIZED PAIN**

**NY 65-15070-100**

10-10-68  
10-10-68  
10-10-68  
10-10-68  
10-10-68

SECRET

CLASSIFIED (b)(7)(C)

**DATE**  
**RECEIVED**

IV 3-17-68 AIR

430

TEACHERS TOTAL DOLLARS \_\_\_\_\_

TEACHER TEST DETAILS \_\_\_\_\_

\_\_\_\_\_

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normal print

Figure 13. DSC-Thermogram of Compound No. 5 (Table 9A):  
Sealed Pan in Nitrogen Atmosphere

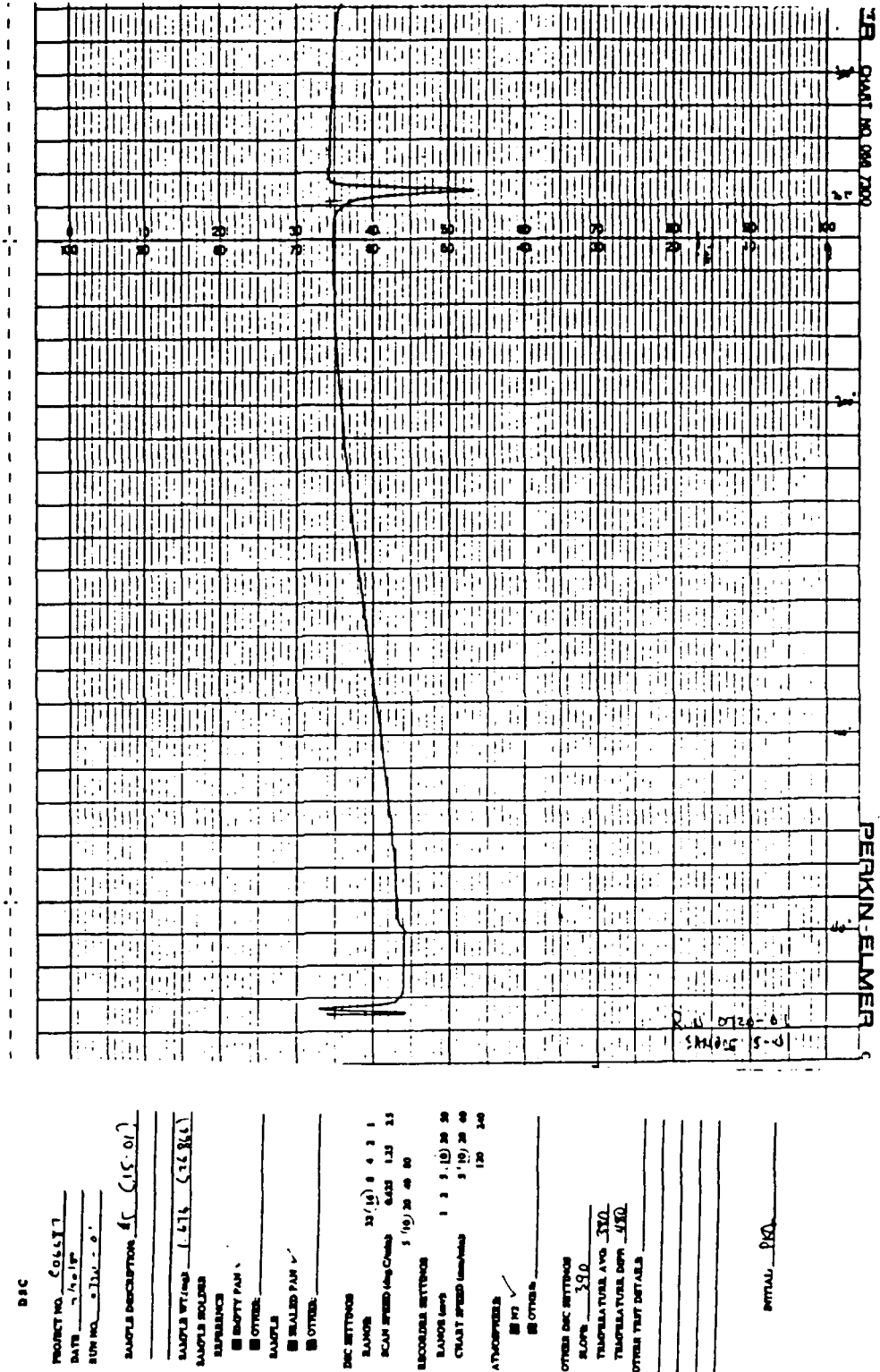
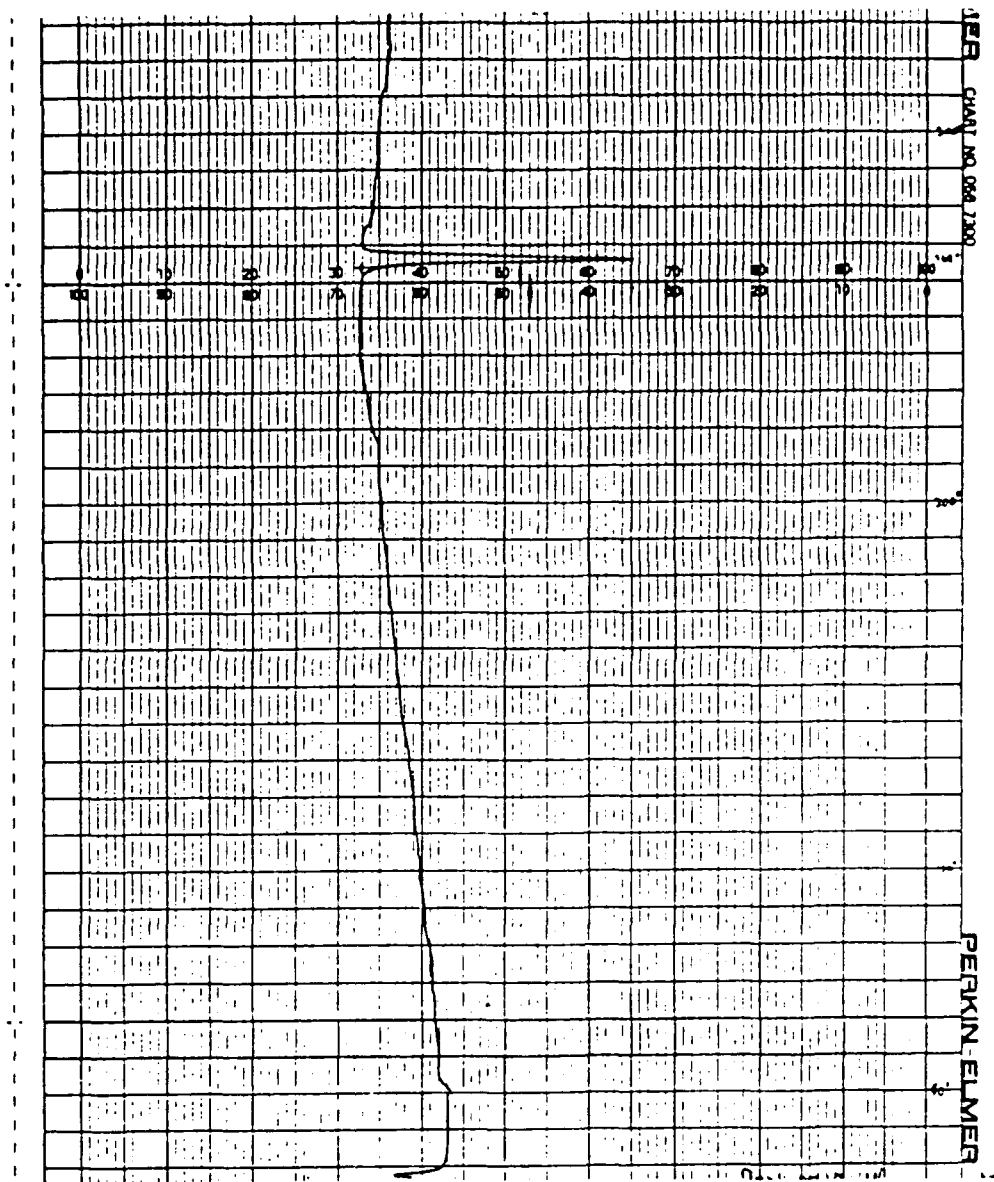


Figure 14. DSC-Thermogram of Compound No. 5 (Table 9A):  
Vented Pan in Nitrogen Atmosphere



BSC

PROJECT NO. 506687  
DATE 7/19/89  
RUN NO. 0114-14

SAMPLE DESCRIPTION #5 (11-04)  
SEMI-SOLID, N<sub>2</sub>

SAMPLE WT/IMP 2.013  
SAMPLE HOLDER  
EQUILIBRIUMS  
☒ EMPTY PAN  
☐ OTHER  
SAMPLE  
☒ SEALED PAN  
☐ OTHER

ATMOSPHERE VENTED NITROGEN PAN

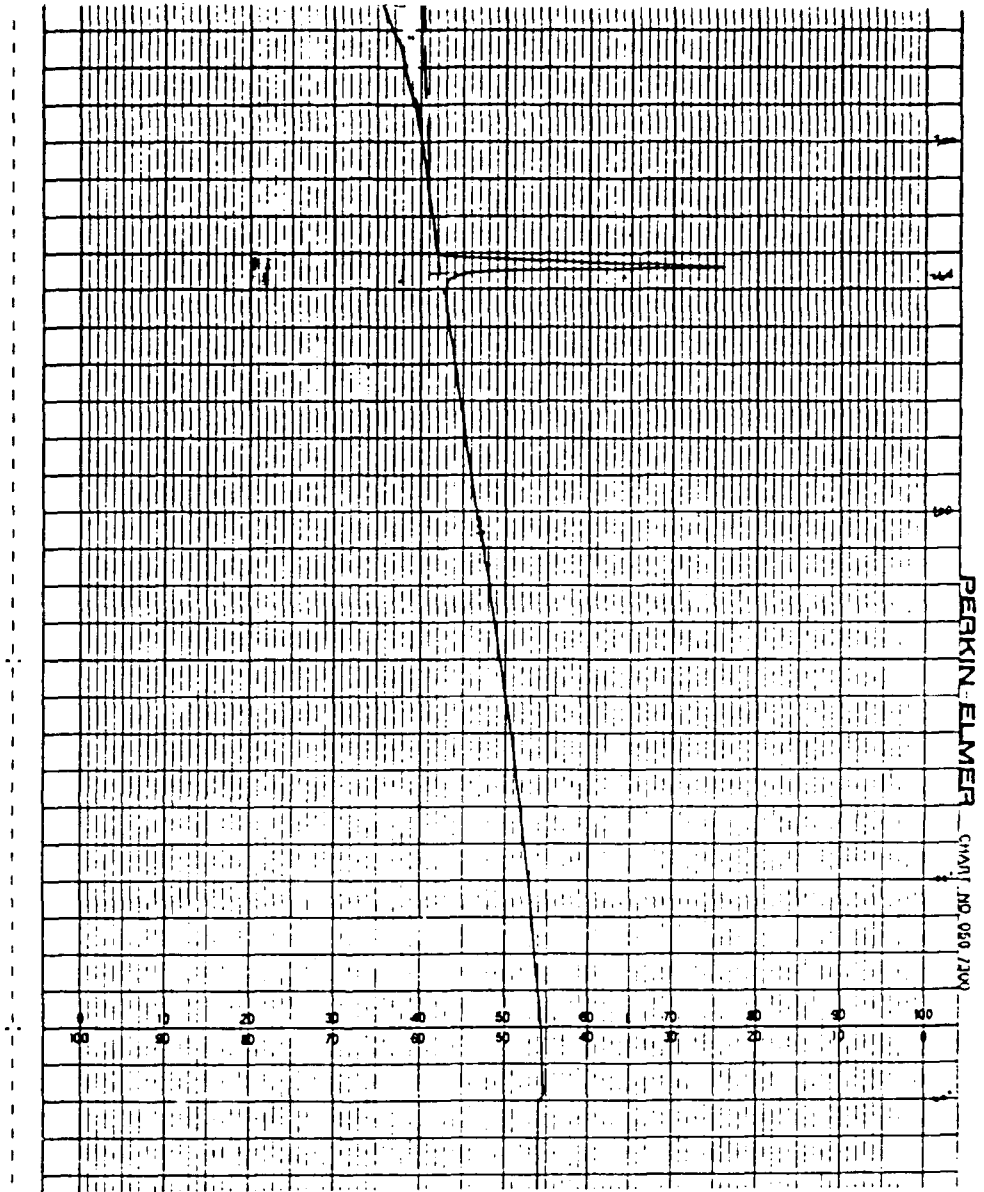
DEC SETTINGS  
BLANKS 12 0 0 0 0 1  
SCAN SPEED (deg/min) 10 10 10 10 10  
RECORDING SETTINGS  
BLANKS 1 1 1 1 1 1  
CRIST SPEED (mm/min) 1 1 1 1 1 1

ATMOSPHERE  
☒ N<sub>2</sub>  
☐ OTHER

OTHER DEC SETTINGS  
SLOP 31A  
TEMPERATURE AND  
TEMPERATURE DEPT  
OTHER TEST DETAILS SCAN RATE 10 deg/min

ANALYST PC

Figure 15. DSC-Thermogram of Compound No. 5 (Table 9A):  
Vented Pan in Air Atmosphere



**DSC**

PROJECT NO. 60437  
DATE 7/11/81  
RPN NO. 0113-01

SAMPLE DESCRIPTION 35 (15-03)  
AIR VENTED

SAMPLE WEIGHT 1.111 (11.111)

SAMPLE HOLDER REPLACEMENT ✓  
☐ BOTT PAN  
☐ OTHER

SAMPLE VENTED VENTED PAN  
☐ SEALED PAN  
☐ OTHER

DSC SETTINGS  
SCAN 1 2 3 4 5 6  
SCAN SPEED (deg/min) 100 120 150 180 200 250

SECURE SETTINGS  
SCAN RATE 1 2 3 4 5 6  
CLOCK SPEED (min/min) 1 2 3 4 5 6

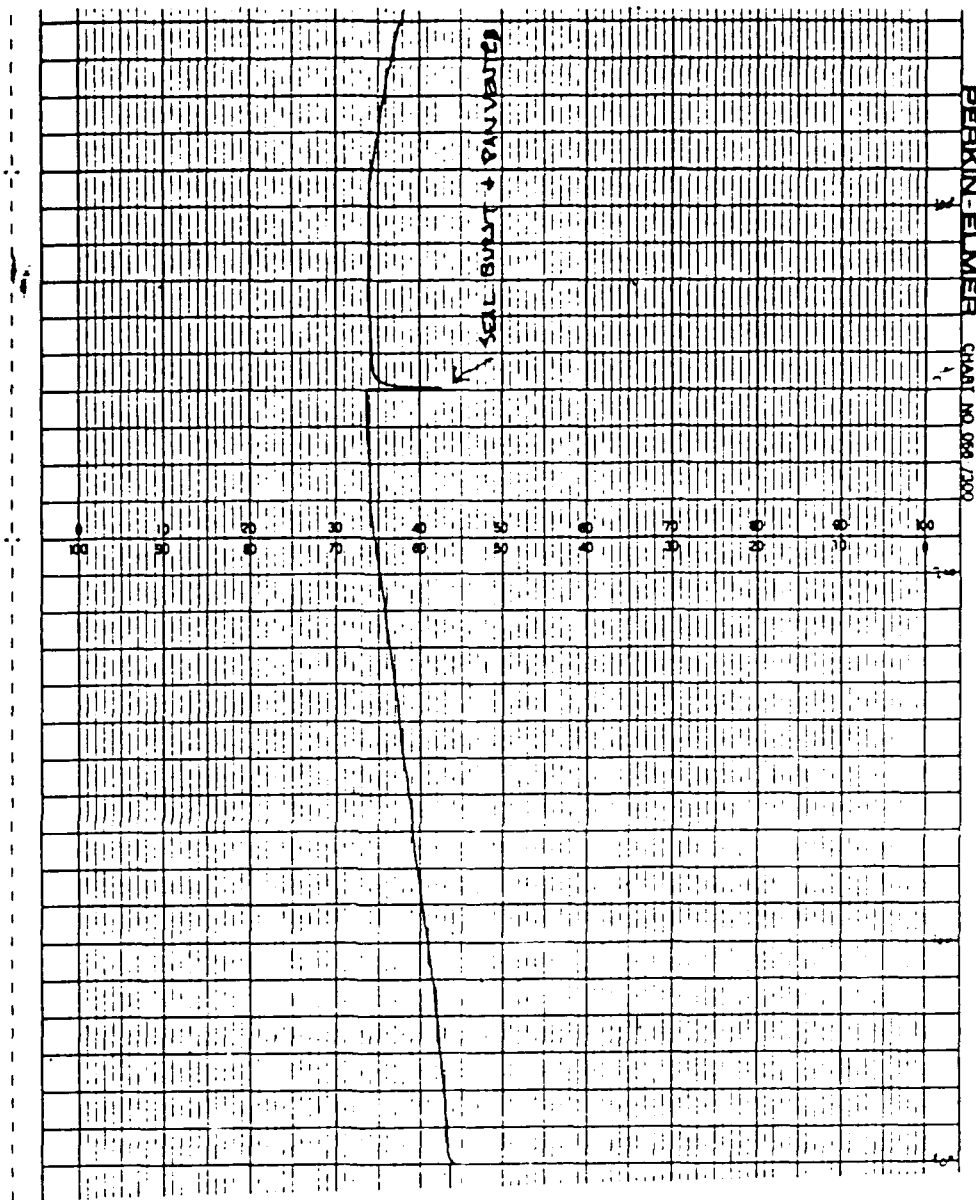
OTHER DSC SETTINGS  
☐ NO  
☐ OTHER TEMP AIR

OTHER DSC SETTINGS  
SLATS 45.0  
TEMPERATURE AVO  
TEMPERATURE BPO  
OTHER TEST DETAILS

DETAIL 1.111



Figure 16. DSC-Thermogram of Compound No. 6 (Table 9A):  
Sealed Pan in Nitrogen Atmosphere



PROJECT NO. C06187  
 DATE 7/10/88  
 RUN NO. AT10-05  
 SAMPLE DESCRIPTION #6 (16-01)  
 SEALING N<sub>2</sub>  
 SAMPLE WEIGHT 2.176 (39.56)  
 SAMPLE HOLDER SEAL  
 PURGENCE N<sub>2</sub>  
☒ BOOTH PAN ✓  
☐ OTHER \_\_\_\_\_  
 SAMPLE SEAL  
☒ SEALED PAN ✓  
☐ OTHER \_\_\_\_\_  
 DSC SETTINGS  
 SCAN RATE 10 1 2 3 4 5 10 20 30 40 50 60 70 80 90 100 120 150 200 300  
 SCAN SPEED (deg/min) 10 1 2 3 4 5 10 20 30 40 50 60 70 80 90 100 120 150 200 300  
 RECORDING SETTINGS  
 SCAN RATE 10 1 2 3 4 5 10 20 30 40 50 60 70 80 90 100 120 150 200 300  
 CHART SPEED (mm/min) 10 1 2 3 4 5 10 20 30 40 50 60 70 80 90 100 120 150 200 300  
 ATMOSPHERE N<sub>2</sub> ✓  
☐ OTHER \_\_\_\_\_  
 OTHER DSC SETTINGS  
 SLOPE 400  
 TEMPERATURE AVO \_\_\_\_\_  
 TEMPERATURE DEF \_\_\_\_\_  
 OTHER TEST DETAILS  
Glitch at 250°C allowed  
Sealed  
 INITIAL PKA

Figure 17. DSC-Thermogram of Compound No. 6 (Table 9A):  
Vented Pan in Nitrogen Atmosphere

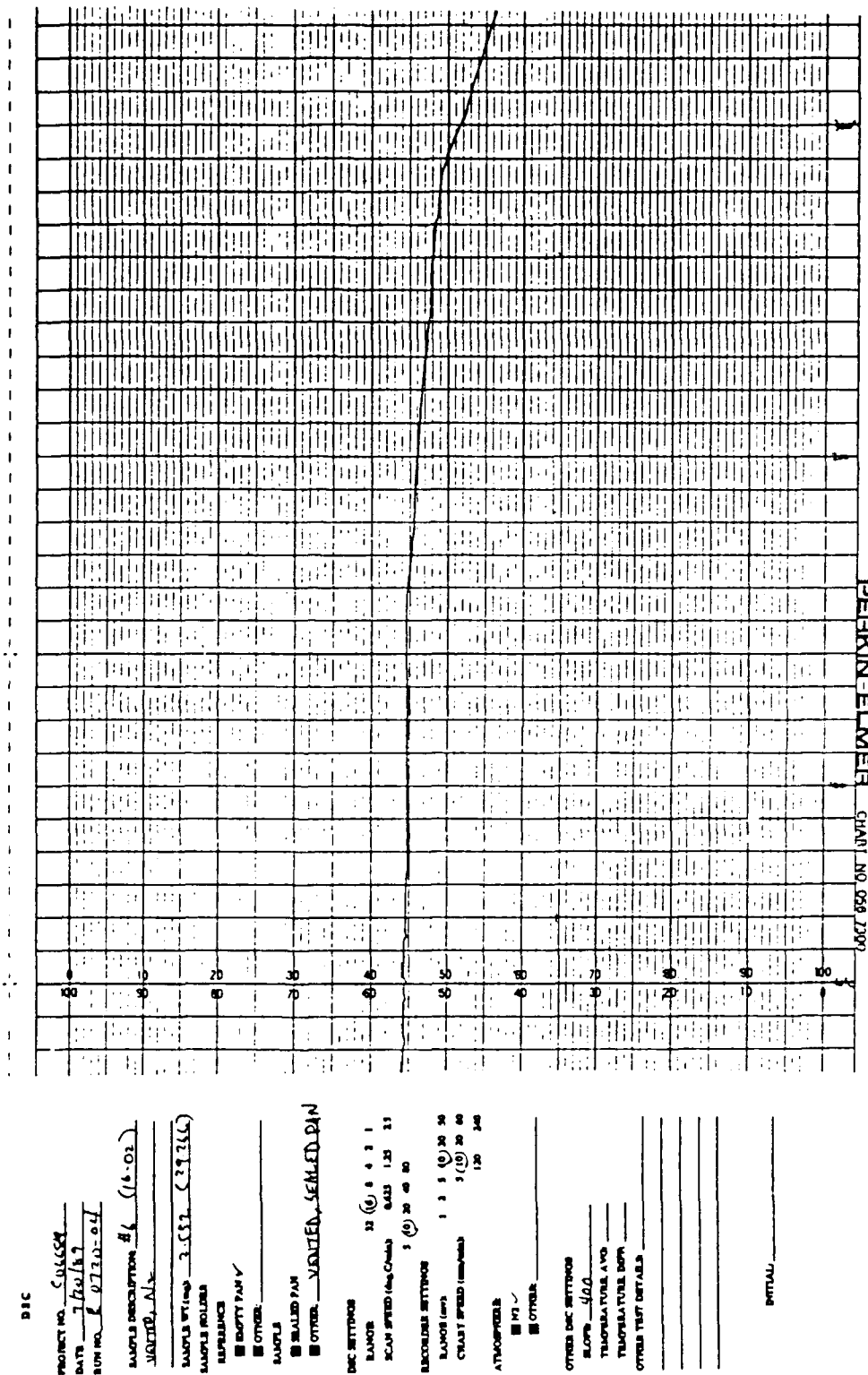
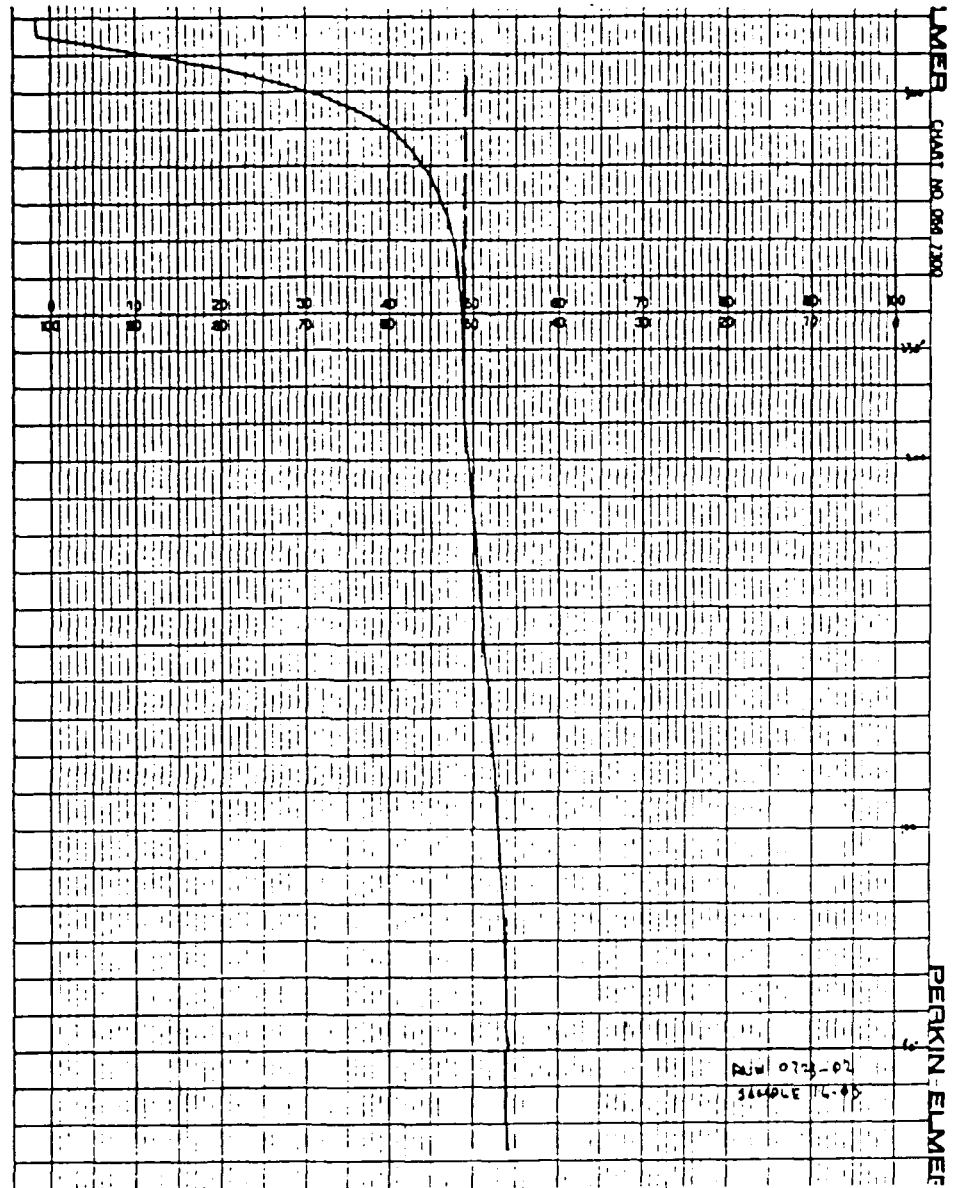


Figure 18. DSC-Thermogram of Compound No. 6 (Table 9A):  
Vented Pan in Air Atmosphere



BIC

PROJECT NO. C06657  
DATE 7/13/82  
BOX NO. 0113-02

SAMPLE DESCRIPTION #6 (1b-D5)  
VENTED AIR

SAMPLE ID TAGS  
SAMPLE NUMBER 1390  
SIZE 100  
TYPE PLASTER  
☒ DUFF PAN ✓  
☐ OTHER

SAMPLES  
☐ SEALED PAN  
☐ OTHER VENTED SEALED PAN

DIC SETTINGS  
BLANK 32 ④ 1 4 3 1  
SCAN SPEED (Avg./Channel) 0.25 L30 LS  
1 ④ 20 40 60

RECORDED SETTINGS  
BLANK 1 3 5 ④ 20 20  
CHART SPEED (mm/min) 5 ④ 20 60  
120 300

ATMOSPHERES  
☐ N2  
☐ OTHER ZERO AIR

OTHER DIC SETTINGS  
TEMP. H2O \_\_\_\_\_  
CIRCULATOR APO \_\_\_\_\_  
TEMPERATURE DIFF. \_\_\_\_\_  
OTHER TEST DETAILS \_\_\_\_\_

INTERNAL DATA

Figure 19. DSC-Thermogram of Compound No. 7 (Table 9A):  
Sealed Pan in Nitrogen Atmosphere

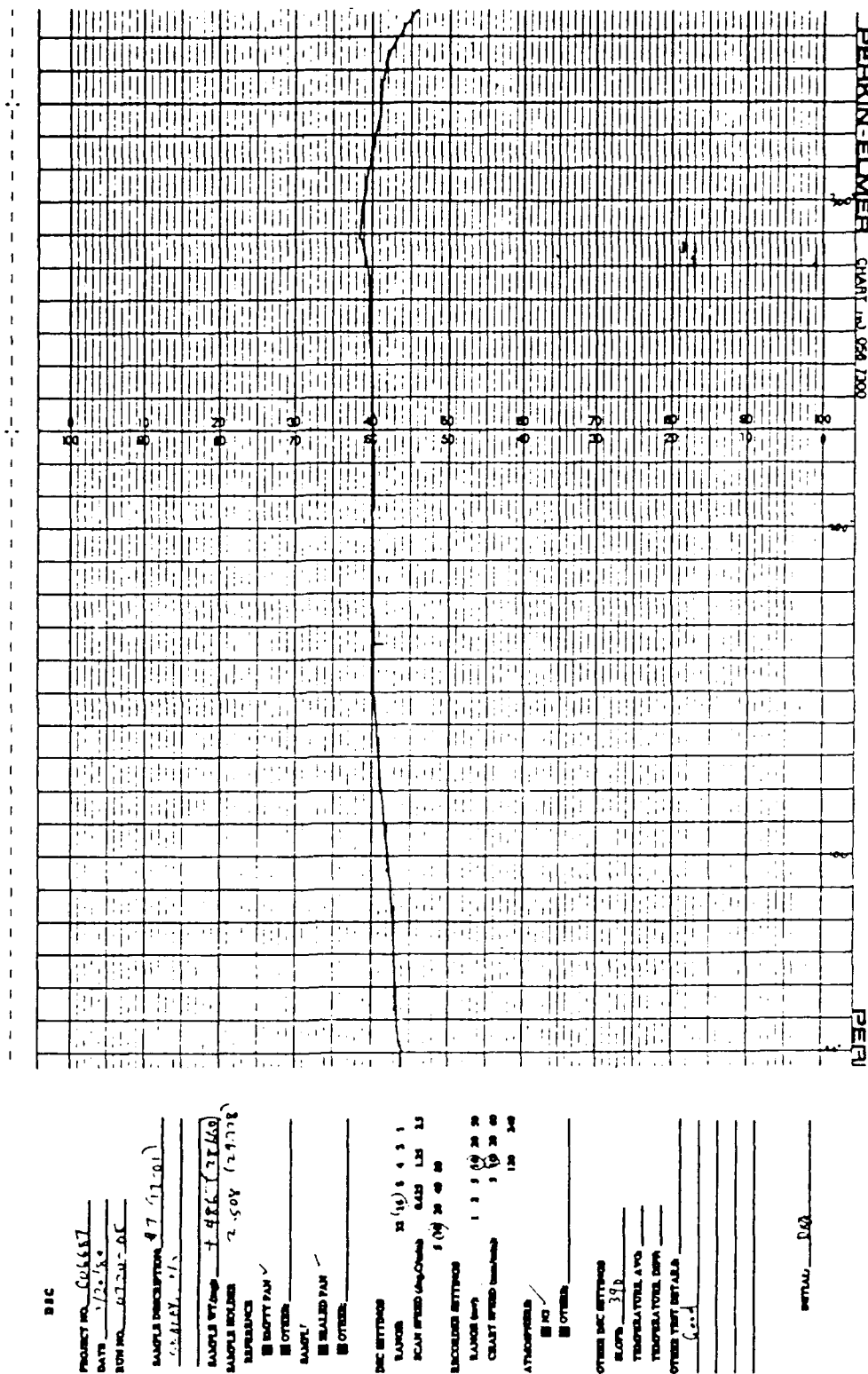
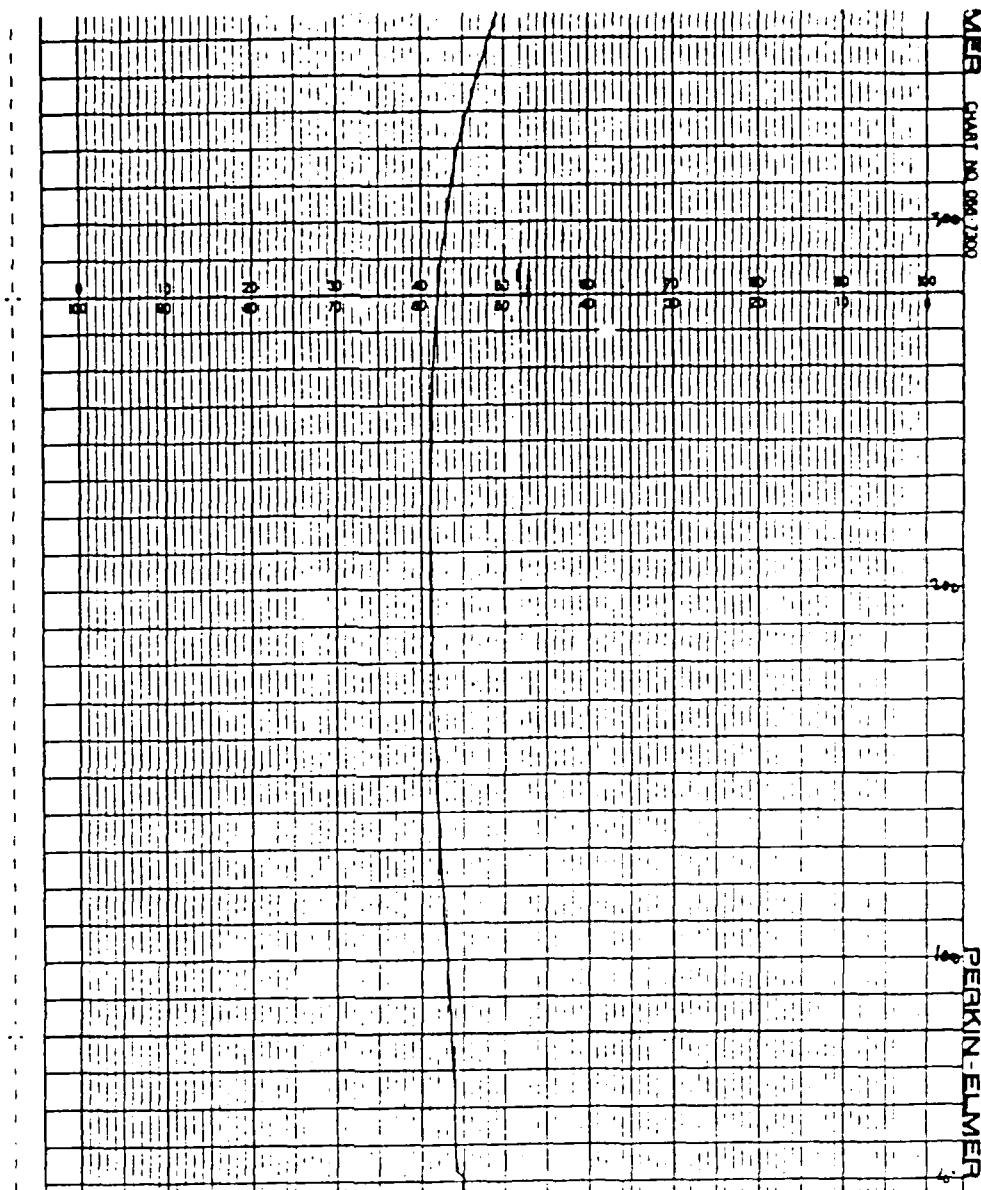
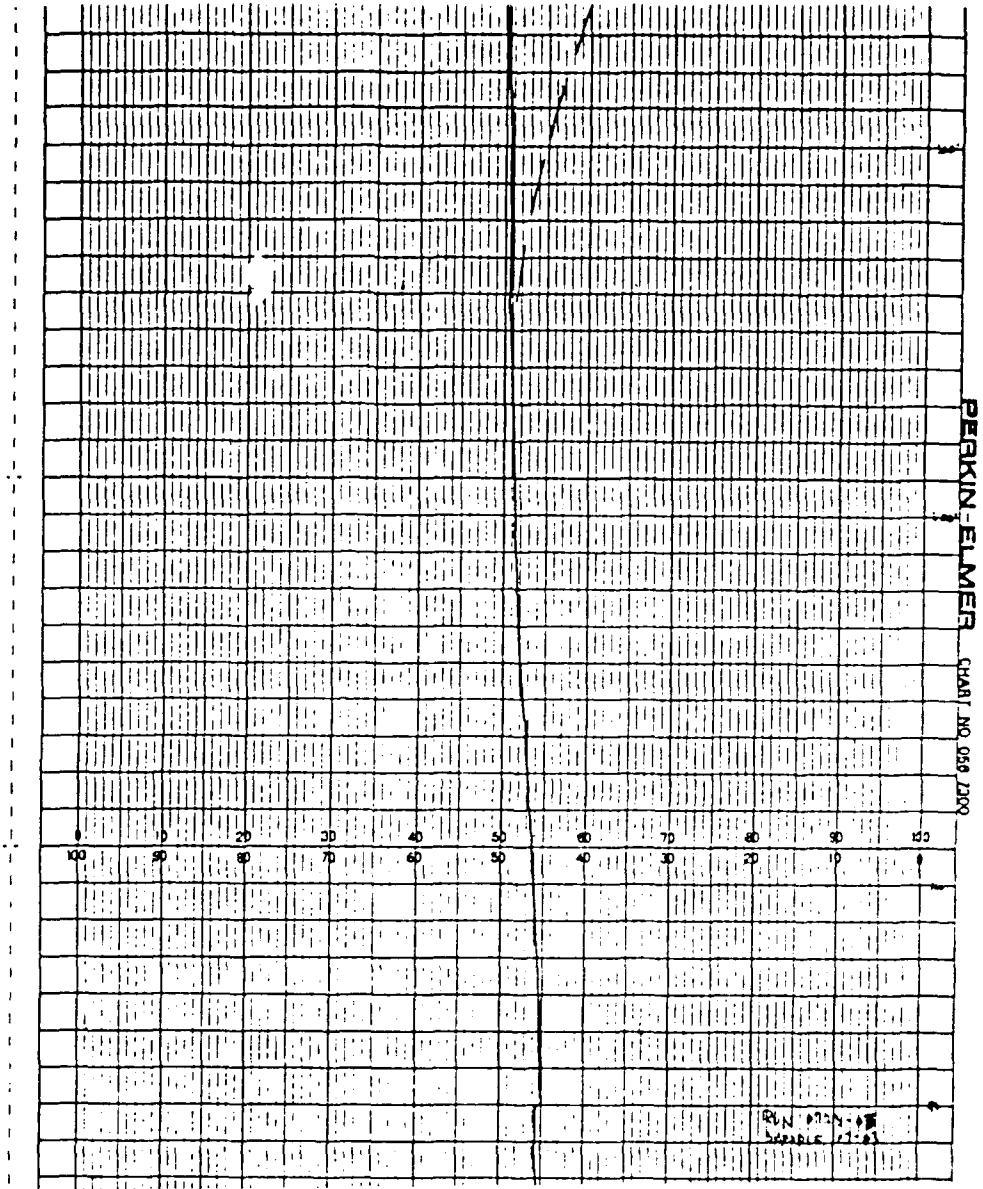


Figure 20. DSC-Thermogram of Compound No. 7 (Table 9A):  
Vented Pan in Nitrogen Atmosphere



DSC  
 PROJECT NO. C-6618-1  
 DATE 1/10/88  
 RUN NO. 0110-1  
 SAMPLE DESCRIPTION #7 (17-02)  
 ANALYST J. J. J. J.  
 1. SAMPLE WT/amp 11.1 (15.34)  
 SAMPLE HOLDER  
 SAMPLES 1  
 SAMPLE PAN ✓  
 OTHER  
 SAMPLE  
 SAMPLE PAN  
 OTHER  
 DSC SETTINGS  
 TANK 10 14 1 1 1  
 SCAN SPEED (deg/min) 10 10 10 10  
 RECORDING SETTINGS  
 TANK 10 1 1 1 1 1 1 1 1 1  
 SCAN SPEED (deg/min) 10 10 10 10 10 10 10 10 10 10  
 OTHER TEST DATA  
 ATTEMPTS  
 10 10 10 10 10 10 10 10 10 10  
 OTHER  
 OTHER DSC SETTINGS  
 SAMPLE 10  
 TEMPERATURE AVO  
 TEMPERATURE BOP  
 OTHER TEST DATA

Figure 21. DSC-Thermogram of Compound No. 7 (Table 9A):  
Sealed Pan in Air Atmosphere



BSC

PROJECT NO. 06687  
DATE 7/13/87  
ROW NO. 0711-03

SAMPLE DESCRIPTION #7 (17-03)  
SEALING AIR

SAMPLE WEIGHT 1.249 (22.937)  
SAMPLE BOLDS  
SAMPLING  
☐ BOTT PAN  
☐ OTHER

SAMPLE  
☐ SEALED PAN  
☐ OTHER VEUTER, SEALED PAN

DSC SETTINGS  
SCAN 10 0 4 2 1  
SCAN SPEED (deg/min) 6.03 1.20 2.5  
3 (9) 20 40 60

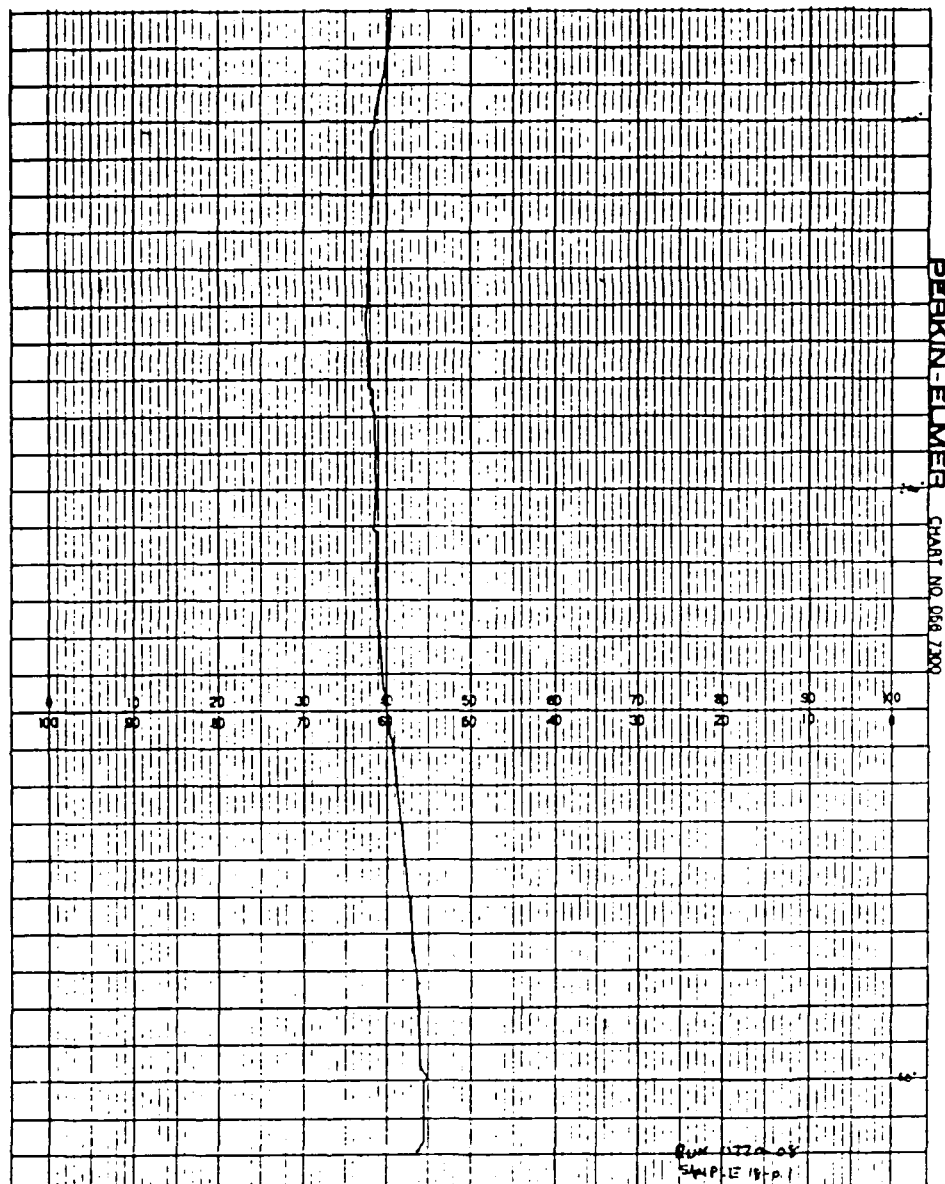
SECURITIES SETTINGS  
SCAN 1 3 1 (9) 20 20  
COAST SPEED (deg/min) 1 (9) 20 40  
120 240

ATMOSPHERE  
☐ N2  
☐ OTHER 15% O2 AIR

OTHER DSC SETTINGS  
SLOPE 13.0  
TEMPERATURE AVO  
TEMPERATURE DEPT  
OTHER TEST DETAILS

DETAIL 24

Figure 22. DSC-Thermogram of Compound No. 8 (Table 9A):  
Sealed Pan in Nitrogen Atmosphere



DSC

PROJECT NO. 001111  
DATE 10/15/84  
RUN NO. 0110-08

SAMPLE DESCRIPTION 15 (18.01)  
SAMPLE NO. 15

SAMPLE WEIGHT 1.3501 (23.571)

SAMPLE HOLDER  
SAMPLING  
SEALING PAN ✓  
OTHER: \_\_\_\_\_

SAMPLE  
SEALING PAN ✓  
OTHER: \_\_\_\_\_

LAC SETTINGS  
SCAN 15 16 17 18 19 20 21  
SCAN SPEED (deg/min) 4.0 1.0 1.0 1.0 1.0 1.0  
SCAN 15 16 17 18 19 20 21  
SCAN 15 16 17 18 19 20 21

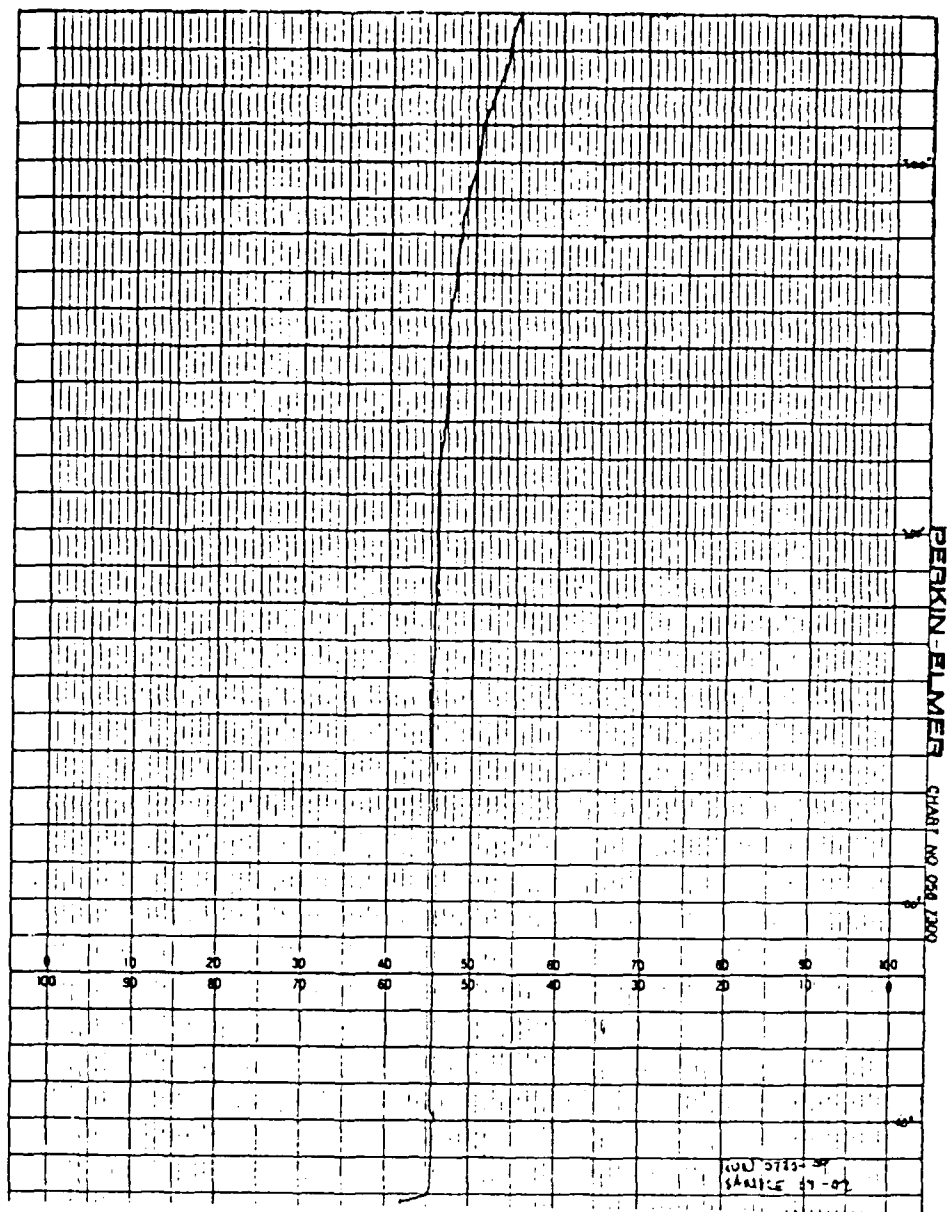
RECORD SETTINGS  
SCAN 15 16 17 18 19 20 21  
SCAN 15 16 17 18 19 20 21  
SCAN 15 16 17 18 19 20 21

ATMOSPHERE  
N2 ✓  
OTHER: \_\_\_\_\_

OTHER DSC SETTINGS  
SCAN 15 16 17 18 19 20 21  
SCAN 15 16 17 18 19 20 21  
SCAN 15 16 17 18 19 20 21  
SCAN 15 16 17 18 19 20 21  
SCAN 15 16 17 18 19 20 21  
SCAN 15 16 17 18 19 20 21

REMARKS Date

Figure 23. DSC-Thermogram of Compound No. 8 (Table 9A):  
Vented Pan in Nitrogen Atmosphere



**DSC**

PROJECT NO. 006487  
DATE 7/1/84  
ROW NO. 0710-09

SAMPLE DESCRIPTION #8 (18.0L)

SAMPLE WEIGHT 2.060 (18.0L)  
SAMPLE HOLDER 2.02.0 (18.0L)  
REPLACEMENTS  
☐ EMPTY PAN ☒  
☐ OTHER  
SAMPLES  
☐ SEALED PAN  
☐ OTHER: VENTED, SEALED PAN

DSC SETTINGS  
SCAN 16 3 4 3 1  
SCAN SPEED (deg/min) 0.425 1.25 3.5  
1 (9) 20 40 60

RECORDING SETTINGS  
SAMPLE SIZE 1 3 5 (16) 20 30  
CHART SPEED (mm/min) 5 (10) 20 40  
120 240

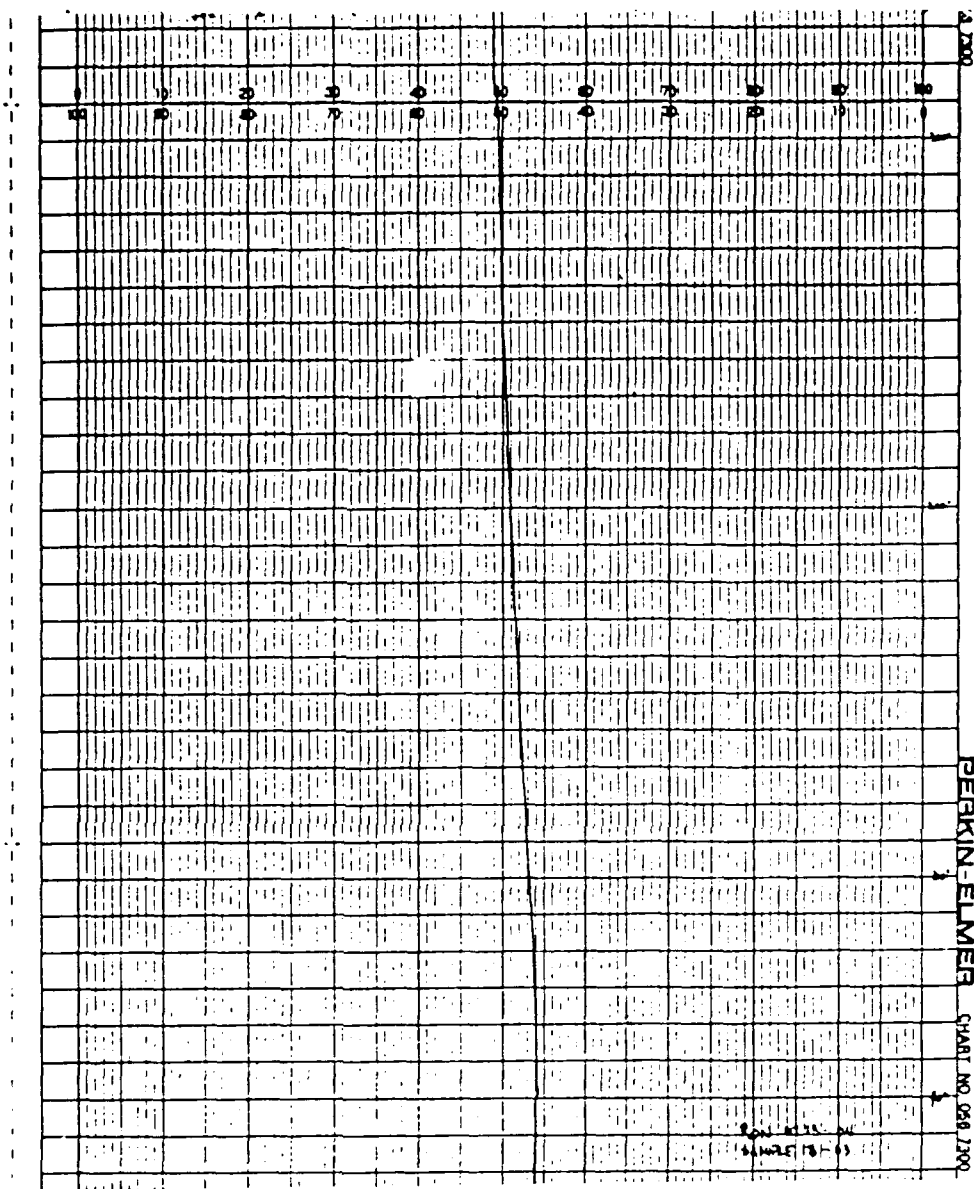
ATMOSPHERE  
☒ NO ☐ OTHER

OTHER DSC SETTINGS  
SLOPE 40.0  
TEMPERATURE A/D  
TEMPERATURE SENS  
OTHER TEST DETAILS

INITIAL YSC



Figure 24. DSC-Thermogram of Compound No. 8 (Table 9A):  
Vented Pan in Air Atmosphere



BIC  
PROJECT NO. 06637  
DATE 1/23/83  
ROW NO. 0723-04  
SAMPLE DESCRIPTION 48 (18-03)  
VENTED PAN AIR  
SAMPLE WEIGHT 24.00 (21.923)  
SAMPLE HOLDER  
EQUIPMENT  
☒ EMPTY PAN  
☐ OTHER  
SAMPLE  
☐ SEALED PAN  
☒ OTHER VENTED PAN  
DSC SETTINGS  
SCAN RATE 10 (10) 1 2 3 4 5 6 7 8 9 10 11 12 13  
SCAN SPEED (μV/min) 10 (10) 10 20 30 40 50  
RECORDING SETTINGS  
SCAN RATE 1 (1) 1 2 3 4 5 6 7 8 9 10 11 12 13  
CRAFT SPEED (mm/min) 10 (10) 10 20 30 40 50  
ATMOSPHERE  
☐ N2  
☒ OTHER ZERO AIR  
OTHER DSC SETTINGS  
RUNS 130  
TEMPERATURE APO  
TEMPERATURE BPO  
OTHER TEST DETAILS

DATE 2/4

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